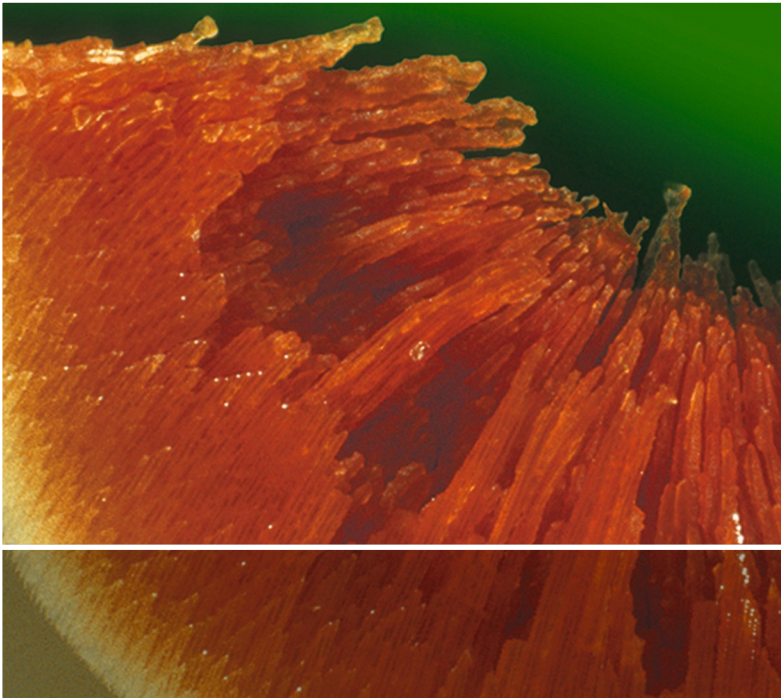


Gottfried Ehrenstein
Sonja Pongratz

Resistance and Stability of Polymers



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Dedicated to our families –
without their patience and understanding
we would not have been able to compile this book

Preface

The resistance of polymeric materials to chemicals and other environmental influences has been covered in a large number of research articles that are typically focused on the behavior of a specific material with regard to a given medium and load. Raw material manufacturers, testing institutions, and users collected vast amounts of singular data both from tailored experiments and from practical experiences.

In 1978, the first comprehensive book covering this topic was published by Dr. Dolezel, supported by C.-M. Meysenbug. Their goal was to provide a comprehensive overview of the behavior of this (then) novel class of materials, including both polymeric materials and elastomers. Although the following years brought numerous new developments, in particular for polymeric materials, this book was never published in an updated, second edition. After many years of extensive research in the field of polymer resistance we came to the conclusion that careful consideration of processing conditions, design, and in particular use and application conditions is necessary before meaningful statements regarding the resistance and stability of polymers can be made. Determining the resistance of polymers is not an exclusively a material science related problem but rather involves all life cycle aspects of a plastic part - from the manufacturing of its raw materials to its end of service life.

With the complexity of this topic, the evaluation of more than 1200 literature references, and our effort to take different perspectives into account, it took 10 years of intensive work to compile this comprehensive and voluminous book. It is great pleasure to see that after more than 30 years, the groundbreaking book by Dolezel and Meysenbug is now available in a current and comprehensive version. However, being well aware of the diversity and complexity of the topic we do not claim completeness. It is our goal for the future to close all existing gaps in the current compilation of data and would like to encourage our readers to provide comments and/or to point out missing information.

The authors wish to express their appreciation to several individuals who provided valuable support and advice during the preparation of this book. Our particular thanks is owed to Prof. Dr.-Ing. Dietmar Drummer and his highly qualified and

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Erlangen/Wolfsburg, Summer 2013

Sonja Pongratz

Gottfried W. Ehrenstein

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■ 1.1 An Introduction to Polymers

By “polymers” we generally mean materials consisting of comparatively simple macromolecular organic compounds. They are manufactured either synthetically or by transforming natural products.

The technically relevant properties of polymers, such as shapability, hardness, elasticity, tensile strength, temperature, and chemical resistance can be varied over a wide range by the selection of raw materials, manufacturing methods, and choice of additives. Polymers are processed further to become molded parts, semi-finished products, fibers, or films.

The reason for the wide variety of polymers is the wide range of monomer building blocks available, as well as the various possibilities for arranging them to form macromolecular chains. Such chains may be linear or branched (thermoplastics) or crosslinked (elastomers or thermosets).

1.1.1 Thermoplastics

Thermoplastics consist of macromolecules physically linked by either linear or branched bonds. Unlike elastomers and thermosets, they are not crosslinked. They are rigid at low temperatures, but when heated they soften to a plastic state in which they can be shaped relatively easily. This process is reversible, i.e., when cooled, thermoplastics resolidify. Between their hard, energy elastic state and their melt state lies their entropy elastic range [1].

In thermoplastic materials, linear macromolecules can align themselves uniformly parallel to one another in microscopic regions and form crystallites, with or without regularly arranged substituents that are not too large. Polymer materials with crystalline regions invariably contain additional amorphous zones where the macromolecules cannot be ordered, which is why they are called semi-crystalline. Besides semi-crystalline materials there are also amorphous thermoplastics [1].

The amorphous state of polymeric materials is characterized by a lack of long-range order, i.e., in submicroscopic zones the macromolecules lack uniform spacing, arrangement, and orientation introduced by the structural arrangement of individual chains [1].

In their entropy elastic region, amorphous thermoplastics are not well suited for structural applications because of their low stiffness and strength properties. The decrease in strength properties is less pronounced in semi-crystalline thermoplastics because their crystalline zones remain rigid and tough until they melt, while only the amorphous zones soften. The degree to which the properties decrease depends on the degree of crystallization. Nonetheless, semi-crystalline thermo-

plastics may be used in the entropy elastic region for structural applications, although some mechanical properties undergo significant changes compared to the energy elastic region [1].

In order to modify the properties of thermoplastics, other materials, such as additives, fillers, and reinforcing agents are added. Moreover, the properties of thermoplastics can be modified by copolymerization (copolymers) or by blending of polymers. Copolymerization creates polymers consisting of two or more types of monomers. Polymer blends are compact material systems consisting of several components whose properties can be differentiated macroscopically [1].

Most polymers used today are thermoplastics. Polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), and polystyrene (PS) often find application as low-end consumer items, packaging or others. Technical parts are produced mostly from acrylonitrile-butadiene-styrene-copolymer (ABS), polyamide (PA), polybutylene terephthalate (PBT), polyoxymethylene (POM), polyether sulfone (PES), polycarbonate (PC), polyphenylene sulfide (PPS), polytetrafluoroethylene (PTFE), polyether ether ketone (PEEK), or polyimide (PI). Polyvinyl chloride (PVC) is a material often used in building construction, especially for roofing membranes, window frames, and pipes, and its properties (rigid or flexible) are generally modified by additives.

By adding energy, these materials can be made shapable or plastic so that they can be processed by various shaping methods, such as injection molding and extrusion. Once the particular component has cooled, it retains its shape. This process is reversible.

Injection molding is a batch process that enables the economical mass production of finished, directly marketable molded parts. Here, the particular material, or molding compound, is plasticized in an injection unit and injected into a mold. The empty space – the mold cavity – determines the shape and surface texture of the finished part. Today, it is possible to produce parts ranging in weight from a few tenths of a gram to double-digit kilograms. Injection molding allows the fast manufacturing of products with high precision, e. g., for mechatronics, in large numbers. Virtually any surface can be created on the part. Smooth surfaces can be produced for optical applications, graining for haptically important areas, as well as patterns and engravings.

When extruded, polymers are squeezed through a die in a continuous process. To do so, the polymer material, or extrudate, is first melted down and homogenized by heat and internal friction in an extruder. Then the pressure on the melt is built up to force it through the die. Once it passes through the die, the polymer material begins to solidify, usually in a water-cooled calibrating unit. Application of pressure forces the material against the calibrating profile. This is often followed by a cooling phase. The cross-section of the resulting geometric body corresponds to that of the die or calibrating unit used.

Examples of products manufactured by extrusion include continuous pipes and profiles with constant longitudinal cross-sections, as well as plastic films of any desired length, which are generally wound into rolls. Plastic containers, such as bottles or cans, and even fuel tanks can be manufactured by extrusion. An extruded preform is enclosed in a mold and pressed against the mold surface by compressed air – a process called extrusion blow molding.

1.1.2 Thermoplastic Elastomers

Thermoplastic elastomers can be described as thermoplastics resembling elastomers, both in molecular structure and behavior. They can melt under the influence of heat, providing a high degree of freedom for shaping during processing; on the other hand, this restricts their use at increased temperatures [1].

Crosslinking in thermoplastic elastomers is not achieved via crosslinking as in conventional elastomers but rather via physical crosslinking by (semi-)crystalline regions, which creates a thermoreversible structure with elastic properties on cooling [1], [2].

The most important examples of thermoplastic elastomers include TPE-O (polyolefin-based TPE), TPE-A (polyether(ester)-block-amide), TPE-E (copolyester-based TPE), TPE-S (styrene copolymer-based TPE), and TPU (polyurethane-based TPE).

1.1.3 Elastomers

Elastomers are highly polymeric, organic materials capable of reversibly absorbing large deformations. This property, together with their potential for absorbing mechanical energy, makes elastomers the material of choice for products that bridge tolerances, permit movements between different components, form both stationary and moving seals, excite and dampen vibrations, and assume spring functions. Typical technical applications include tires, seals, conveyor belts, V-belts, hoses, rubber springs, elastic couplings, cable jackets, roof membranes, shoe soles, and many others [2].

Elastomeric or rubber materials result from the wide-mesh crosslinking of amorphous, thermoplastic precursors (natural rubber). These weak chemical bonds between polymer chains result in typical rubbery, highly elastic behavior above the glass transition temperature [2].

Prior to any forming process, various components are added to the natural rubber material during mastication; they include vulcanizing agents, fillers, plasticizers, anti-aging and processing agents. The number of these added components can be significant and their quantity may well exceed that of the natural rubber [2].

Unlike thermoplastics, the shaping process for elastomeric materials is coupled with a chemical reaction that results in crosslinked rubber parts [2].

Elastomers are subdivided into various classes:

- **R class** elastomers have backbones consisting exclusively of carbon atoms, some of which are connected by double bonds (reactive sections). These double bonds enable crosslinking with sulfur, but are simultaneously sensitive to attack by oxygen and ozone. Examples: natural rubber (NR), nitrile rubber (NBR), styrene-butadiene rubber (SBR)
- **M class** elastomers contain only C atoms and no double bonds in their backbones; this improves aging resistance. Examples: ethylene-propylene rubber (EPDM), acrylate rubber (ACM), fluoro rubber (FKM)
- **O class** elastomers contain oxygen (O atoms) in addition to C atoms in the backbone, but do not exhibit double bonds. Example: epichlorohydrin rubber (ECO)
- **T class** elastomers contain sulfur (S atoms) in the backbone in addition to C atoms. Example: polysulfide rubber (T)
- **U class** elastomers contain nitrogen (N atoms) and oxygen (O atoms) in addition to C atoms in the backbone. Example: polyurethane elastomers (AU, EU)
- **Q class** elastomers have main chains consisting of oxygen (O) and silicon (Si). Example: silicone rubber (Q)

1.1.4 Thermosets

Thermoset materials differ from the much larger group of thermoplastics in the way they are processed as well as in their properties in general, especially their aging behavior.

The great majority of thermosets serves as matrix material for fiber-reinforced (FRP) or filled plastics. Consequently, they can be found in structural components, e. g., as interior and exterior paneling for vehicles, in boats, and wind energy rotors, as well as in classic light-weight design (aerospace, racing). Moreover, they are often used for large-scale components in plant and building construction (flue gas scrubbers, sewage treatment plant covers, chemically resistant pipes). They are not commonly used for mass-produced articles, because they are less profitable to produce than thermoplastics. Examples of thermoset applications can be found in areas with demanding requirements, e. g., regarding insulation potential or dimensional stability at elevated temperatures, such as in housings for electronics or motor vehicle engine parts. Non-fiber reinforced resins serve as embedding and coating material. In their pure form, thermosets exist only in niche applications, such as lenses for eyeglasses.

While thermoplastic materials, chemically speaking, remain one and the same material prior and subsequent to melting and processing, the final, solid material of thermoset parts is created during manufacturing from their non-polymeric, generally fluid or liquefiable base components.

For condensation reaction thermosets, this chemical reaction during processing includes the elimination of low-molecular by-products, while the processing of reaction polymerization resins does not result in such elimination. To initiate the curing reaction, curing agents, e. g., catalysts and promoters, are required in addition to the resin. These components are generally mixed in at the time of processing; storage-stable, commercial pre-mixed formulations are sometimes used. The final product after the curing process is a material that is three-dimensionally crosslinked, infusible, and insoluble in solvents.

The class of reaction resins includes unsaturated polyester resins (UP) and vinyl ester resins (VE), whose oligomers (linear base molecules) are dissolved in styrene. When a catalytic amount of curing agent is added, these mostly fluid resins copolymerize in radical polymerization while opening their double bond with the styrene. Epoxy resins (EP) represent another important group of products. EPs are oligomeric, solvent-free systems with either terminal or central epoxy rings. Stoichiometric addition of a hydrogen donor (e. g., amines, acid anhydrides) initiates the polyadditive curing process, forming a 3-dimensional network). Depending on resin type, the cure of reaction resins is either heat- or mixing activated.

Phenolic resin (PF) is the technically most important representative of the class of condensation resins. It is created in several process steps from the monomer base materials carbolic acid and formaldehyde. Here, we distinguish between resols and novolacs. Phenolic resins are often processed in the form of free-flowing molding compounds under pressure at elevated temperatures; individual cases of liquid processing are also known. Melamine resins, urea resins, and furan resins are also condensation resins created from formaldehyde.

Included among the thermosets in a wider sense of the term are certain silicones, methacrylate, and polyurethane as well as additional special materials groups (bismaleimide, diallyl phthalate, etc.).

1.1.4.1 Epoxy Resins (EP Resins)

Uncured EP resins range from liquid to solid at room temperature and may also contain additives, such as solvents. Their molecules have at least one, in most cases two EP-groups that are required as functional groups in order to build macromolecules. The curing component is supplied in liquid or powder form; it contains active hydrogen atoms in the molecule that react with the EP-groups of the resins in a polyaddition reaction [3], [4]. EP resins are high-quality thermosets with good mechanical properties as well as high dimensional stability and adhesion to sub-

strates. Only 8% are used in the production of fiber-reinforced applications; further important applications include casting material for electronics, mold resins and coatings of all kinds, especially in the form of powder coatings.

EP resin systems consist of resin and curing agent molecules reacting with each other in approximately the same quantities, whereas in unsaturated polyester resins, the curing agent is only a source of free radicals and added in catalytic quantities. Therefore, EP resins and curing agent also have to be mixed together in strict stoichiometric proportions. Because resins and curing agent are also based on different chemical compounds (amines, acid anhydrides, phenols, etc.), EP-systems are a widely varied class of materials.

Polyaddition, in contrast to radical catalytic reaction, is not a chain reaction in which a few chains grow quickly. Instead, numerous resin molecules react comparatively slowly with the curing agent molecules, so that the molecular weight increases only slowly. Thus, the resin mixture will remain liquid although many resin-curing agent bonds have already formed.

In contrast to polyester resins, liquid EP resins are not provided in solvent solution (exceptions: paint and coating systems) and are usually more viscous than polyester resins. Solid EP resins are melted at elevated temperatures in order to process them. In the fiber-composite sector, both their price and their better mechanical, especially dynamic properties destine them for high-end applications, sometimes with carbon fiber reinforcements as in aeronautics and racing. Often prepregs, i. e., pre-impregnated reinforcing materials, are processed using autoclave technology, combining elevated temperature, pressure, and local vacuum. Although prepregs have a rather short shelf-life, it is important to maintain reproducible quality of the prepregs to ensure optimum composite properties after curing. For large GFC-structural components manufactured by resin infusion technology, newly developed resin/curing agent systems with low viscosity provide good fiber impregnation as well as long open times and low exothermics. Their good adhesion to metal and good insulating properties predestines EP resins to serve as highly mineral-filled casting material in the electronics industry.

To a large degree, the curing agents (available in numerous variants) control the final properties and are usually tailored to specific applications. Many different resin properties can be set by selecting suitable epoxies, curing agents, and additives, Table 1.1.

Resin property		Achievable via resin building blocks	Achievable via additives
Processing relevant	Low viscous	“Long-chain” curing agent (rotor blade hardener)	Reactive thinner
	Thixotropic	Less so	Highly disperse silicic acid
	Fast curing (i. e., short open time)	Curing agent	Accelerator
	Long open time	Curing agent	Less so
	UV-curing	Cycloaliphatic resin	Photoinitiators
Relevant for thermal/mechanical properties	High heat distortion temperature	Highly reactive resin, e. g., based on novolac	Less so
	Flexible	Long-chain resin	Polyols and other flexibilizers
	Chemical resistant	Highly reactive resin, e. g., based on novolac	Less so
Relevant for long-term behavior	Lightfast	Cycloaliphatic resin	UV absorber
	Flame retarded	Phosphoric EP resins	Bromine compounds (with antimony trioxide), phosphorous, aluminum trihydroxide

Table 1.1 *Modifications to influence the properties of EP resins*

Fiber composites with EP resins as matrix resins are used for high-quality composites for aerospace and sports applications and in electronics – thanks to their good insulating properties they are optimally suited for circuit boards. In addition, rotor blades for wind-power systems beyond a certain size that cannot be made from UP resins are another area of increasing demand.

Table 1.2 provides an overview of various resin-curing agent systems for FCP-applications. A wide variety of base components can be used to create numerous EP systems (cold- or self-curing as well as heat activated curing systems) to meet any given requirement. Glass transition temperatures beyond 200 °C are attainable, significantly higher than those for UP- and VE resins.

As with other resin classes, there are flexibilized and flame-resistant grades as well as epoxies modified with rubber particles that exhibit increased toughness without significant decrease in heat resistance.

Good adhesion and low shrinkage are the reasons for the excellent mechanical properties of EP molding materials, especially their dynamic behavior.

Thanks to their high quality, EP resins are also often used as matrix for expensive fibers, e. g., as CFC in airplane construction. In order to assure precisely reproducible laminate structure, mostly epoxy prepregs are used for high-quality applications.

Table 1.2 Comparison of properties for various EP resins for FCP; T_g = glass transition temperature, σ_{ts} = tensile strength, E_0 = Young's modulus, ε_B = ultimate strain

Property						Comment
Liquid resin		Cured resin				
Basis	Mixing viscosity (mPa·s) 25 °C	T_g (°C)	σ_{ts} (N/mm ²)	E_0 (N/mm ²)	ε_B (%)	
1) Bromated EP resin solution	2,100–2,900	135–140	—	—	—	FR4 product for prepregs and laminates; printed circuit boards
2) Bis-A-EP resin with formulated amine curing agent	5,200–6,000	185–195	110–120	2,800	5.5–6.5	System with good hydrolysis resistance
3) Cycloaliphatic resin with anhydride curing agent and imidazol accelerator	150–250	188–193	48–65	3,050	1.8–2.5	Low viscosity system with high heat resistance for filament winding, pultrusion etc.
4) Bis-A-EP resin with anhydride curing agent and imidazol accelerator	600–900	145–153	80–90	3,200	5.0–7.0	Anhydride curing standard system mainly for filament winding, pultrusion etc.
5) Formulated resin with cycloaliphatic amine curing agent	500–700	143–148	71–77	2,600	4.5–5.5	Processible by RTM, winding, pressing, laminating etc.
6) Toughness modified EP resin with amine curing agent	720–860	100–110	120–130	2,800	9.0–12.0	Good fracture mechanical properties
7) Formulated, amine cured EP system	320–380 350–400	90–105	125–130	2,900	7.0–12.0	Low viscous, flexible system for industrial applications
8) Formulated EP resin with curing agents based on aliphatic polyamines	300–400	70–74	3.8–4.2	3,200	10.0–13.0	System for laminating large components (e. g., wind rotor blades), adjustable reactivity
	550–800	82–86	4.0–4.4	3,500	5.2–5.8	
	1,000–1,200	85–90	4.4–4.9	3,700	5.0–6.2	

Table 1.2 Comparison of properties for various EP resins for FCP; T_g = glass transition temperature, σ_{ts} = tensile strength, E_0 = Young's modulus, ε_B = ultimate strain (Continued)

		Property				Comment
Liquid resin		Cured resin				
Basis	Mixing viscosity (mPa·s) 25 °C	T_g (°C)	σ_{ts} (N/mm ²)	E_0 (N/mm ²)	ε_B (%)	
9) Formulated EP system	200 – 300	80 – 85	74 – 78	3,300	5.8 – 6.2	System for infusing large components (e. g., wind rotor blades), adjustable reactivity
	220 – 230	80 – 85	77 – 81	3,300	7.2 – 8.0	
10) Modified, solvent-free resin with expanding agent; polyamine curing agent	–	125 – 127	–	–	–	Standard product for expandable epoxy systems applications
11) Formulated expanding EP system	–	125 – 135	–	–	–	Low-emission, expanding epoxy system, specifically for the automotive industry
12) Hydrocarbon epoxy novolak resin with aromatic amine curing agent	2,290 (79 °C)	210	135	3,100	–	Aeronautics applications, especially suitable for resin film infusion processes
13) Tetrafunctional EP resin with aromat. polyamine curing agent	7,000 – 19,000 (50 °C)	236	90	3,400	2.0 – 3.0	Multifunctional high-performance resin for prepreg formulations
14) 2-Component bismaleinimide system	800 – 1,000 (100 °C)	290 – 300	176	3,400	5.0 – 8.0	System for very high service temperatures
15) Cyanate ester monomer	100	240 – 260	162	2,900	3.0 – 4.0	Aeronautics application

The relatively high viscosities compared with UP resins make fiber impregnation more difficult at lower temperatures. However, new, low viscosity resin systems have been developed especially for new infusion techniques for large components with long impregnation paths. The use of reactive thinners and solvents is declining because they are considered health and ecological hazards.

Reaction times for EP resins are generally longer than for radical curing systems (UP-VE resins). Although accelerators are used also for self-(cold) curing systems, influencing the curing reaction with the help of curing agents, accelerators, and inhibitors, as is commonly done with UP resins, has only very limited effects here. Temperature-step programs are thus usually used for accelerated yet low residual stress curing. With these programs, reaction is started at a low temperature. The only slightly crosslinked resins can partially relieve residual stresses caused by reaction shrinkage by relaxation. This effect is reinforced by subsequent heating until curing has progressed at a rate that is increased by elevated temperatures. Residual stresses can be minimized analogously by implementing temperature-step programs during cooling.

At 2 to 5%, volume shrinkage in EP resins is comparatively low. Since most of the shrinkage occurs in the liquid phase, it can be further compensated by additional inflowing resin.

If each resin molecule reacts with a single curing agent molecule, a large amount of possible reactions and the accompanying shrinkage take place without any essential increase in molecule size or increase in viscosity. After approx. 50% of potential reactions, the resin compound will gel and no longer be free-flowing.

The degree of crosslinking at the gel point is to some extent dependent on the functionality of the epoxies; i. e., resins with molecules that carry many EP groups (= functional groups) will gel sooner than so-called low-functional EP resins.

During copolymerization of oligomers and chain or network formation, as during the polymerization of UP and VE resins, the resin mixtures may have gelled after little more than 10% of potential reactions. This prevents stress relaxation by inflowing resin mass. Shrinkage and shrinkage related residual stresses cannot relax and thus have clearly more significant effects.

EP systems polymerizing by polyaddition contain a much smaller number of potential reactions sites in the solid state than UP and VE resins, therefore they shrink significantly less. However, EP curing times are longer than those for UP and VE resins. The finished parts thus exhibit lower residual stress, higher strength, and higher dimensional accuracy than parts made from UP molding materials.

Like all reaction resins, EP resins cure without elimination of by-products. Other than acrylate and polyester resins, they also do not contain monomers that cause intense odor. Both resins and amine curing agents pose a health hazard. When

laminated in open molds and/or during handling of liquid resins, skin irritations and allergies are known to occur.

As a rule of thumb, cold curing with alkaline reactive amines leads to EP resin parts that are quite resistant to alkali, but less resistant to acids; on the other hand, acid and hot water-resistant parts with high heat distortion temperatures result from heat activated curing with acid hydrides, although they are not particularly alkali resistant. Alkali and acid resistance is better balanced when aromatic amines are used for curing.

Special properties of EP resins include

- high-quality resins, approx. 3 to 4 times more expensive than UP resins,
- stoichiometric dosing of resin-curing agent is required,
- very good mechanical, especially dynamic properties, therefore predestined as matrix for high-quality fibers (e.g., C fiber), good adhesion to many substrates (glue),
- comparatively high viscosity and slow curing reaction, less flexible processing behavior than UP and VE resins,
- chemical resistance depends on curing agent (amines – alkali resistant, acid anhydride – acid and hot water-resistant),
- spectrum of temperature resistance broader than for UP/VE (T_g above 200 °C),
- occasional skin irritation and allergies caused by liquid resins,
- brand names: Araldite (Huntsman Advanced Materials), Epicote (Resolution Performance Products), Dow Epoxy Resins “D.E.R.” (Dow Chemical), Rütapox (Bakelite AG)

Most EP resins are based on bisphenol-A, resins based on (cyclo)aliphatics are less commonly used. Aliphatic EP resins are not particularly high-temperature molding materials, but especially interesting when low processing viscosity or high resistance to aromatics is required. Once they are cured, aliphatic EP resins form rigid thermosets. Curing is initiated by specific amounts of curing agent that may reach levels high enough that they affect the chemical resistance more than deviations in the resin-curing agent ratio. Unlike with polyester resins, processing time cannot be controlled during the polyaddition reaction via the amount of curing agent due to the predetermined stoichiometric ratio.

The most important EP classes are bisphenol-A and novolac resins; the latter are characterized by a large number of EP groups per molecule and result in highly crosslinked molding materials with high heat distortion temperatures. Cycloaliphatic EP resins exhibit low viscosity and, in contrast to aromatic epoxies, are UV stable and thus suitable for outdoor applications. In addition to the usual material data, EP processing resins are characterized by their EP equivalent, which provides information on how many EP groups per unit weight are available – high crosslink-

ing can be assumed for high equivalents. This and additional characteristic data are used to calculate the stoichiometric mixing ratio of resin and curing agent:

- EP equivalent: resin weight (g) that contains 1 mol EP group,
- EP value: number of mol EP groups in 100 g resin,
- H-active equivalent: curing agent weight (g) that contains 1 mol of active hydrogen.

$$\text{EP value} = \text{H-active equivalent} = \text{curing agent (g) per 100 g resin}$$

1.1.4.2 Phenolic Resins (PF Resin)

PF resins are reaction resins manufactured by condensation polymerization of phenols and aldehydes, especially formaldehyde, in aqueous solutions (30 to 50%). Variations are based on different phenolic base materials, different phenol-formaldehyde ratios, and on different chemical or physical modifications, Table 1.3.

Resin property		Achievable via resin building blocks	Achievable via additives
Processing relevant	Low viscous	Low molecular resin	Water
	Thixotropic		Borates, cryolite
	Low in emissions	Resin with low monomer content	Alkaline hardening
	Fast hardening (or short drop times)	Many reactive groups	Acid catalysis resorcinol
	Long drop time	Few reactive groups	via pH
Relevant for thermal mechanical properties	High heat distortion temperature	Increases network density	
	Flexible	Partial replacement of phenol by ortho- or para-alkyl phenol, etherification of the methylol group, incorporation of elastomer building blocks	Dispersion rubbers
	Chemical resistant	Etherification of the phenolic hydroxyl groups	
Relevant for long-term behavior	Light resistant	Amines	
	Flame retardant	Self-extinguishing	

Table 1.3 *Modifications to influence PF resin properties*

For phenol-formaldehyde molar ratios with a formaldehyde surplus of 1:1.2 to 2.5, resoles are created under alkaline condensation; for a formaldehyde deficiency of 1:0.5 to 0.9, novolacs are created under acid condensation. During the formation of phenol oligomers, both acid and alkaline catalysis eliminate water as a condensation product, Figure 1.1.

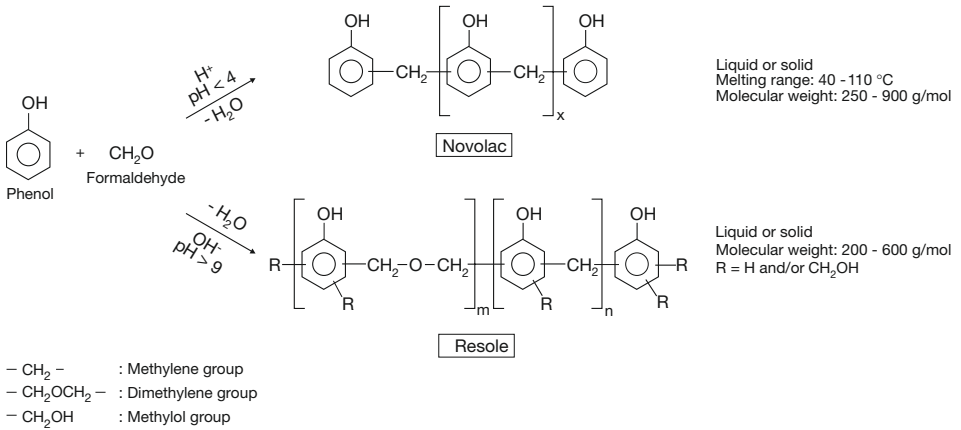


Figure 1.1 Production of resoles and novolacs through conversion of phenol and formaldehyde

The average molar mass of phenol-novolac resins is approx. 250 to 900 g/mol, i. e., approx. 4 to 10 phenol groups. Resoles are liquid or solid with a softening temperature as high as approx. 70 °C. The median molar mass of liquid resoles is approx. 300, that of solid resoles approx. 400 to 600 g/mol [5].

Phenol and formaldehyde are crosslinked to form novolacs or resoles via a polycondensation reaction. During the reaction cleavage products, such as water or ammonia are released. Although the reaction is exothermic, the endothermic evaporation of water (condensation product, viscosity reduction of liquid resoles) may cause a cooling effect. However, the entire heat-initiated curing process is an exothermic process that requires significant cooling. After curing, PF resins form high-molecular resite, Figure 1.2, which is neither soluble nor fusible.

The curing process of PF resins is chemically and thermally complex, characterized by endo- and exothermic sequences. During initial heat input, the free water begins to evaporate at approx. 60 - 80 °C in appreciable quantities. Simultaneously, the non-cured material begins to soften, linked to increasing molecular movement in the chains. Both process steps are endothermic and completed at approx. 110 °C. Next is an initial strong exothermic crosslinking reaction up to approx. 160 °C.

The liquid, i. e., pourable resoles contain reactive methylol groups that are heat and acid activated and thus can be crosslinked by heating (which is common practice) or by adding acids.

They are self-curing and thus not storable. The heat-curing sequence of resoles is a very complex reaction in which mainly methylene and dimethylene bridges develop. At temperatures above 160 °C, the dimethylene bridges are also transformed into methylene bridges under cleavage of formaldehyde. The formaldehyde leads to additional crosslinking [5], [6].

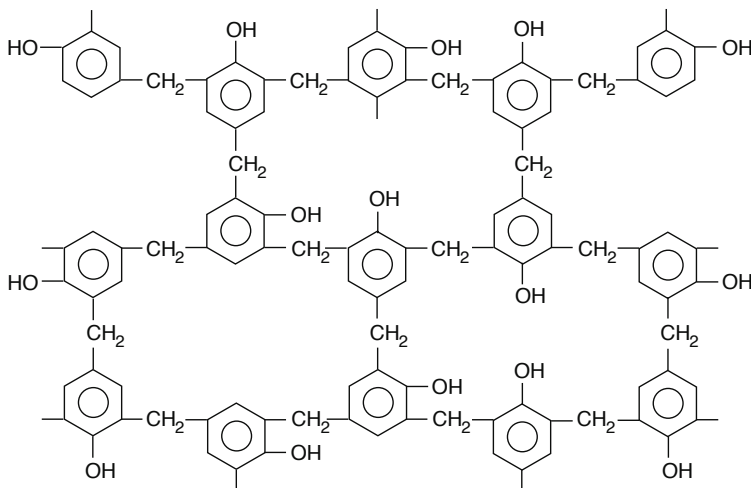


Figure 1.2 Polymer structure (resite) of cured PF resins

The mostly solid (or powdered) novolacs have no heat-reactive groups and thus have to be cured by adding curing agents at elevated temperatures. Without curing agents, they exhibit thermoplastic behavior. The most common crosslinking agent is hexamethylene tetramine – also known as “Hexa”. Hexamethylene tetramine starts to degrade at 110 °C, initiating the curing process of the molten novolac powder and the cleavage of ammonia. Covalent bridges (dimethylene amine and trimethylene amine bridges) develop, resulting in crosslinking. Above 170 °C, a second exothermic reaction occurs when nitrogen containing bridges rearrange to form methylene bridges, releasing ammonia in the process. The curing process of novolacs is therefore described as a two-stage reaction. The softening temperature, characterized by glass transition, is increased to over 200 °C as curing is completed. Thermal degradation of PF resins begins at 280 – 300 °C. Novolac-hexa mixtures cure faster than resoles.

We distinguish the following reaction states during the crosslinking of PF resins:

- A-state:** Linear initial state; resole or novolac; liquid or solid; meltable and soluble
- B-state:** Not clearly defined interim state, also termed “resitole”; meltable and still shapable when heated; insoluble, but swellable; low mechanical strength,
- C-state:** Final state, also termed “resite”; unmeltable, insoluble; high mechanical strength and chemical resistance.

Acid-curing resoles can be processed by hand-lamination, spray-up lamination, winding, and by infusion-technology, as well as by processes familiar from fiber-composite polymer (FCP) technology. Acid-resistant machine components and molds have to be used, and the shorter open times compared to polyester resins have to be taken into consideration. Compression processing, which is suitable for novolacs and resoles, requires ventilation strokes – as in most processing methods with closed molds – to let the developing water vapor escape.

PF resins are brittle and have to be modified for most structural applications. Phenol derivatives, such as alkylphenols and bisphenol A, can be used for this purpose. Co-curing of PF resins with EP resins has proven successful. Here, two preregs can be molded simultaneously when the crosslinking reactions are linked by suitable curing parameters. Elastomer modified PF resins are also used. A large number of PF resins and other formaldehyde-based thermosets, such as amino resins (urea and melamine resins), are compression and injection molded as molding compounds with filler and reinforcing materials. Even though injection molded fiber-reinforced PF resins have gained a firm foothold in applications under the hood, the lion's share of molding compound applications contain wood flour, mineral flour, cellulose fiber, or fabric cuttings and thus cannot be directly classified as fiber reinforced plastics. PF resins are also used as binding agents for insulation materials (sound and temperature insulation) and wood materials (weather-proof chipboard and fiberboard), for abrasive tools and disks, as well as in the friction pad industry (brake pads) and for commutators in electric motors.

The percentage of PF resins among the classic fiber reinforced plastic materials is comparatively small. Although they can be processed by a number of common methods, their use is limited, because they form volatiles during curing and are generally too brittle to be used as structural components. Their outstanding features, besides high chemical and thermal resistance, are innate flame resistance, as well as very low smoke density and low smoke toxicity in case of fire. That is why they are in increasing demand as composite materials in the interior of planes, trains, and other commercial vehicles.

PF resins, especially those containing novolacs, turn brown under UV light and can change color during curing. Therefore, they are manufactured in dark, muted color shades.

The special properties of PF resins are:

- They account for only a small segment of the classic fiber-composite materials;
- Acids (resoles) and cleavage products can complicate processing;
- High heat and chemical resistance, as well as dimensional stability;
- Advantageous fire behavior with retained strength (use in vehicles);
- Brand names: Rutaphen; Bakelite® (Bakelite AG); Askofen (Ashland-Südchemie-Kernfest AG); Uravar (DSM Resins B. V.).

1.1.4.3 Unsaturated Polyesters (UP Resins)

Most unsaturated polyester resins (UP resins) are colorless to slightly yellowish solutions in reactive solvents that are curable both at room temperature as well as under heat without releasing volatile byproducts. During curing, reaction heat is released and the volume decreases by 5 to 9%. The resins consist of oligomeric linear molecules with reactive double bonds. These highly viscous resins are dissolved in styrene, which simultaneously acts as a comonomer for curing. They are subject to a radical curing mechanism. Due to their low viscosity and good fiber wetting ability, their high and/or flexibly adjustable curing rate and comparatively low price, they are often the materials of choice for fiber composite applications [3], [4].

UP resins have been known since 1936 and have certainly gained the widest application as composite materials; more than 70% of all the unsaturated polyester produced goes into fiber composite processing. There are numerous resins with a wide variety of properties. The properties are controlled by the type of molecular building blocks, because unsaturated polyester resins are formed by the reaction of dicarboxylic acids (e. g., ortho-, iso-, terephthalic acid, fumaric acid, maleic acid) with glycols (e. g., 1,2 propylene glycol, neopentyl glycol). Besides maleic acid or its anhydride, phthalic acid anhydrides are especially important because of their low price. Whereas orthophthalic acid improves processing properties and increases chemical resistance, the use of tetrahydrophthalic acid creates particularly tough and heat resistant materials. High quality and hydrolysis resistant molding compounds often consist of isophthalic acid or terephthalic acid. Dicyclopentadiene (DCPD) is often chosen as an inexpensive, readily available raw material and is used together with unsaturated acids and glycols for fiber reinforced applications with low fiber print, especially in boat construction.

The length and number of double bonds in the polyester chains play a role as well as other molecular details, such as flexible units. A UP resin is the more reactive, the greater the proportion of polymerizable double bonds in its initial components. As reactivity increases, the crosslinking density during copolymerization, the nascent heat, and the shrinkage increase. Such highly reactive resins exhibit a high glass transition temperature and good stiffness as well as strength. Because of the high number of crosslinking points, they require heat for curing and/or post-curing at elevated temperatures to ensure sufficient molecular motion. Crosslinking density may also be controlled via the degree of curing.

However, it is good practice to make sure UP resin molding compounds are completely cured to avoid changes in the molded part during service (subsequent shrinkage, moisture absorption, chemical attack, etc.). The curing process of most UP resins at room temperature is significantly delayed by the influence of atmospheric oxygen. Uncovered surfaces remain tacky.

Resin viscosity is largely dependent on the styrene content, which usually ranges from 30 to 50%. The processor may increase the styrene content to a certain extent in order to lower the viscosity of the resin and make the resin easier to process and ensure that the fibers are well wetted; however, excess styrene tends to embrittle the cured material.

The properties of UP resins can be largely varied by the selection of initial components and the choice of additives. This is true for both processability and properties of the molding compounds. Additives are often used as fillers and to lower the price. They typically increase viscosity, thus impairing flowability and processability. Important fillers include chalk, china clay, and aluminum hydroxide. The latter mainly reduces flammability and is added at a ratio of 1:1. The advantages of fillers are reduced shrinkage (increased dimensional stability during processing) and a lower thermal coefficient of expansion (increased dimensional stability in service) [7].

The properties of UP resins can also be precisely controlled via their molecular building blocks and additives, as illustrated in Table 1.4. Typical properties of different UP resins created from various initial components are shown in Table 1.5.

Resin property		Achievable via resin building blocks	Achievable via additives
Processing relevant	Low viscous	Low-molecular resin	High styrene content
	Thixotropic	Less so	Highly dispersive silicic acid
	Low emissions	Less so	Paraffin
	Fast curing (or short open time)	Less so	Accelerator
	Long open time	Less so	Inhibitors
	UV curable	Photo-reactive functional groups	Photoinitiators
Relevant for thermal mechanical properties	High heat distortion temperature	Highly reactive, high molecular resin, e. g., based on isophthalic acid + neopentyl glycol	Less so
	Flexible	Rather low reactive resin; based on adipic acid + triethylene glycol	
	Chemical resistant	Highly reactive resin, e. g., based on isophthalic acid + neopentyl glycol, cyclical diols	
Relevant for long-term behavior	Lightfast	Less so	UV absorber
	Flame retardant	Less so	Aluminum trihydroxide (with antimony trioxide) chloroparaffin

Table 1.4 Modifications to influence UP resin properties

Base	Property					Properties/applications
	Viscosity (mPa · s)	HDT/ T_g (°C)	σ_{ts} (N/mm ²)	E_0 (N/mm ²)	ε_B (%)	
Orthophthalic acid, standard glycols	540 – 610	63/93	70	4,300	2.0	Low to mid-reactive, used for a wide range of stress-free laminates, boat construction
Orthophthalic acid, standard glycols	700 – 900	90/122	85	4,400	2.4	Mid- to highly reactive, low stress cracking tendency; for tanks, pipes, compressed parts
Orthophthalic acid, standard glycols	240 – 290	108/130	80	3,470	4.2	Highly reactive, low viscous; good impregnation when hand laminated and injected, high filling levels possible
Dicyclopentadiene	450 – 1,000	70/-	66	3,500	3.0	Good wetting, little fiber print; e. g., for boats
Terephthalic acid	430 – 580	125/-	60	3,350	2.1	High temperature-stable; for glass fiber reinforced tanks, pipes etc. for hydrocarbons
Maleic acid, standard glycols	1,150 – 1,400	145/-	55	3,400	1.7	Base resin for low-profile SMC (Class A)
Isophthalic acid, standard glycols	3,000 – 3,600	130/150	60	3,700	1.8	Highly viscous SMC-/BMC resin; good hydrolysis resistance

Table 1.5 *Properties of various UP resins; HDT = heat distortion temperature according to DIN EN ISO 75-1/2. T_g = glass transition temperature, σ_{ts} = tensile strength, E_0 = Young's modulus, ε_B = strain at break*

To improve chemical resistance and other properties, UP resins with particularly long-chain UP, i. e., increased molecular weight, are used. With standard, orthophthalic acid-based resins this is not easy to achieve, other than with resins based on iso- or terephthalic acid. Such highly condensed resins require styrene contents of approx. 45 wt.%, instead of the usual 35 wt.% common for standard resins, and are still quite highly viscous for processing.

The molecular mass of UP is not listed in product specifications, but with unfilled resins it can be determined from resin viscosity and styrene content. Medium condensed isophthalic acid resins usually result in final properties worse than those of orthophthalic acid resins with the same degree of condensation.

Even though the improvement in hydrolysis resistance is much increased by increasing molecular mass, UP resins do not really become alkaline resistant until the ester bonds are protected by a hydrophobic spatial shielding ("sterically hin-

dered"). This is usually achieved by including special glycols, such as neopentyl glycol or alkoxyated bisphenol A. The influence of these glycols is stronger than the effect achievable by specially modified acids such as *het-* or *isophthalic acid*.

For some of the most important chemical media, lists of chemical resistance properties (see appendix) indicate which resin types are suitable for which temperature range, but they do not reveal which of the resin types listed is most resistant [8]. Thus, there are cases in which inexpensive orthophthalic acid resins are clearly superior to so-called chemical resistant special resins; and this is the case even if only hydrolysis resistant special resins are considered.

There simply is no universally chemical resistant UP resin. Moreover, they are resistant either to alkalines or aromatics only.

UP resins cure by radical copolymerization of the resin molecule double bonds with those of the styrene molecules. Organic peroxides (R-O-O-R) are used as radical donors that form radicals (RO·) under the influence of accelerators and/or heat. These radicals can open double bonds that will react further. The radicals proliferate in a chain reaction. Curing rate can be influenced over a wide range via temperature and especially by addition of curing agents and accelerators; in principle, the same resin system can cure within a few minutes or over several days. To obtain a long processing time, inhibitors are added that intercept the radicals, thus delaying the curing reaction.

Protection against media influence is required especially for the glass fibers in composites. If coating with thermoplastic film (thermoplastic linings) is technically or economically not feasible, so-called chemical barrier layers are applied, i. e., pure resin layers (fine layers) or layers reinforced with thermoplastic fibers or glass mats, depending on the load experienced and the protection required [7], [8].

Barrier film layers are approx. 0.5 mm layers of resin applied to the mold, containing no fiber material and as little filler as possible. The barrier layers of resin (which do not have to be identical to the laminating resins) have to meet special requirements. To prevent them from running off sloping surfaces, they should be set thixotropically. This increases processing viscosity and prevents the creation of harmful air bubbles, but has a mainly negative effect on chemical resistance. Chemical barrier resins have to cure quickly in order to avoid loss of styrene, which will increase the risk that they will not dry on well; this can be checked with a cotton swap dipped in acetone. When wiped over the surface, insufficient curing is indicated by a tacky surface. It is possible to differentiate between good and optimum curing by lightly polishing the surface with P360 or finer wet abrasive paper and water. If the polished area exhibits the odor of bitter almond or benzaldehyde, curing is not optimum. Also, the gel coat has to be sufficiently cured to withstand the effect of the styrene from the laminating resin without swelling. Therefore, UP

chemical barrier layers have to be highly reactive, i. e., they exhibit a high crosslinking density and thus tend to be brittle and susceptible to cracking [9].

Chemical barrier layers can be reinforced with synthetic fibers or glass fiber non-wovens, which has the advantage that their thickness can be more easily maintained and wet-on-wet lay-up is possible; however, the protective barrier layer is thinner. Besides these thin barrier layers, random oriented fiber layers (at least 2.5 mm thick) may also be employed. The various possibilities are listed in DIN 18820 Part 3, which also recommends suitable layer structures for various chemicals [8].

Finishing coats are also fine barrier layers, but applied as the last layer rather than the first one. Because they have to cure in air, UP resins remain tacky due to the influence of atmospheric oxygen, have an unpleasant odor, are not weather resistant, and swell up with a whitish color in rain.

EP resins are an alternative that cure tack-free. Solvent-containing paints may also be suitable, if the coating layer adheres sufficiently and is resistant. However, paints contain solvents that may evaporate so that other solvents, e. g., from the UP resin laminate, can penetrate the remaining structure and subsequently diffuse out slowly and influence environment or stored goods in containers made from UP laminates. Cold set laminates should be post-cured soon after production to ensure that the reaction agent is still effective.

1.1.4.4 Vinyl Ester Resin (VE Resin)

VE resins differ from UP resins in that only terminal methacrylate groups provide for crosslinking and ester bonds exist only there. In bisphenol A-based VE resins, this principle makes the molding material very tough with rather good alkaline resistance, but a somewhat lower heat distortion temperature because of the double bonds. VE resins based on phenolic resin components are decidedly more reactive, as well as of low viscosity and highly crosslinkable due to their shorter molecular chains. They exhibit optimal heat distortion temperatures, but are relatively brittle and thus similar to molding materials from UP resins based on proxylated bisphenol A. They do not quite achieve the same resistance to alkalis, but are also resistant to aromatics.

VE resins, also known as phenacrylate resins (PHA resin), are similar to UP resins insofar as they are processed analogously. They are usually dissolved in styrene, contain reactive double bonds, and cure radically with addition of peroxide. However, these resins are not formed by dicarboxylic acids and glycols, but from epoxy and acrylic or methacrylic acid. Corresponding to the two commercial epoxy types, bisphenol A and novolac, there are bisphenol-A epoxy VE resins and novolac epoxy VE resins, see Figure 1.3. In both epoxies, terminal double bonds crosslink with styrene to form the final molding material.

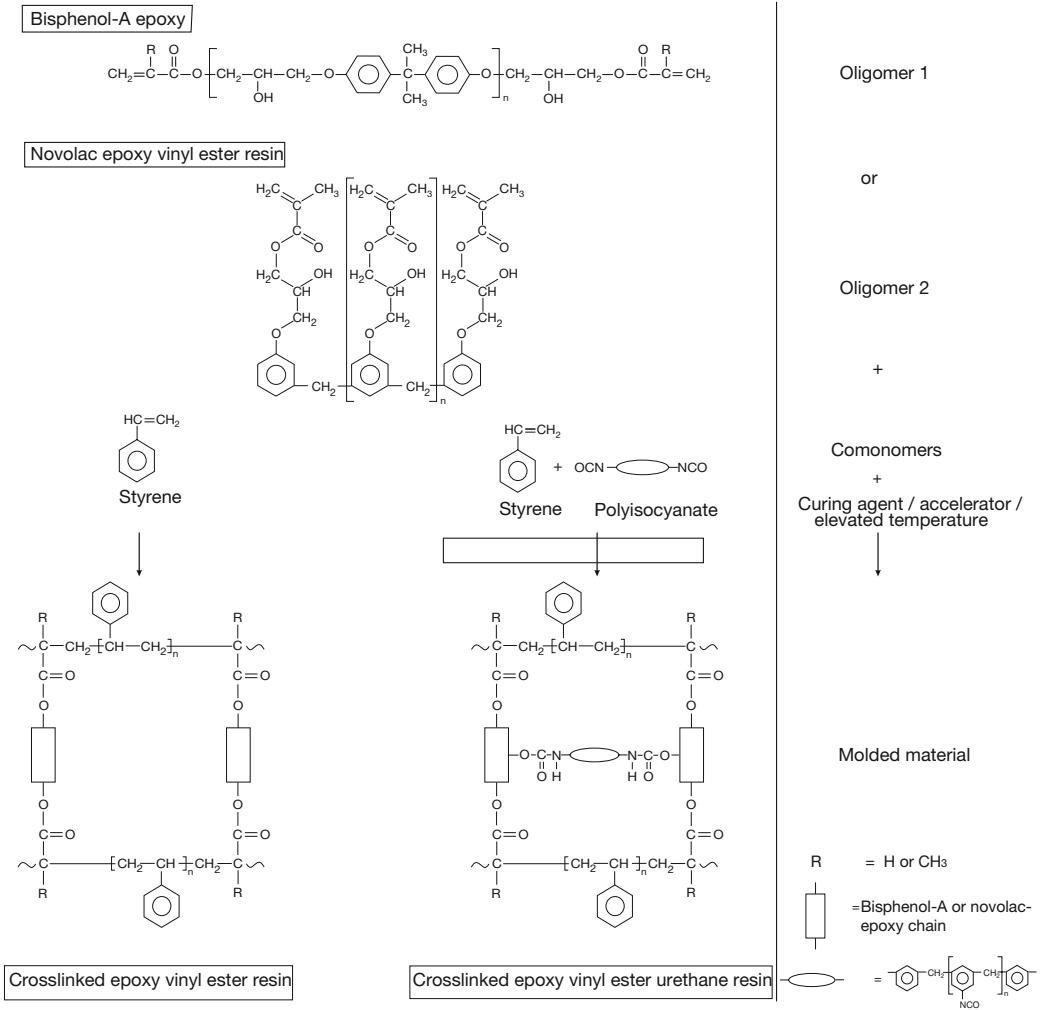


Figure 1.3 Curing of various VE resins and vinyl ester urethane resins (VEU resin)

A newly developed third class of vinyl ester resins is represented by the even higher quality VE urethanes based on bisphenol A epoxy. Here, the secondary OH groups of the VE react in polyaddition with polyisocyanates to produce urethane bridges, see Figure 1.3. Vinyl ester urethane resins (VEU resin, vinyl ester urethane-hybrid resins) combine the good mechanical properties (stiffness) of VE resins with excellent high-temperature resistance (T_g approx. 220 °C and HDT approx. 210 °C) and excellent chemical resistance (the long-term durability of VEUH resin exceeds that of normal VE).

The urethane groups in the chain provide thixotropability and good (glass)fiber wetting. However, VE urethanes are measurably more brittle and absorb more water than normal VEs because of the reactive isocyanate groups [9], [10]. Two

features characterize the advantages of VE resins over UP resins: they are clearly tougher and they exhibit higher chemical resistance. The entire molecule can lengthen under mechanical load, since their double bonds, and consequently their crosslinking points, are at both ends of the VE molecule chains, whereas in UP resin they are distributed over the entire molecule chain. Thus VE resins exhibit elongation at break higher than 6% and very high toughness. The ester groups are also terminal, making the resin chemical resistant. The epoxy portion of VE resins is responsible for their high heat distortion temperature. Compared to EP resins, VE systems have the advantage of easier processing due to their low viscosity and rapid, controllable curing reaction. As with the UP resins, a wide range of various types of VE resins is available, Table 1.6.

Property						Properties/application
Liquid resin		Cured resin				
Base material	Viscosity (mPa · s)	HDT/ T_g (°C)	σ_{ts} (N/mm ²)	E_0 (N/mm ²)	ε_B (%)	
Bisphenol A epoxy	440 – 500	105/130	95	3,600	6.1	Medium reactive; for tanks, pipes, sewer retrofit
Bisphenol A epoxy	360 – 400	105/130	95	3,600	6.1	Medium reactive, reduced styrene emission
Bisphenol A epoxy	650 – 750	107/132	90	3,800	3.9	Very good mech. properties and chem. resistance; prepregs for waste water sewer retrofit, UV curing
Bisphenol A urethane	400 – 500	115/132	83	3,500	4.2	Highly temperature and chemical resistant (alkali), thixotropable, compatible with aramid fibers; winding, centrifugation, spray lay-up
Flexibilized bisphenol A urethane	400 – 500	125/-	85	3,300	5-6	Extremely temperature and chemical resistant with high flexibility, very good fiber wetting; winding (tanks), centrifugation
Novolac epoxy	210 – 280	140/150	90	3,500	4.0	Heat and corrosion resistant; tanks, pipes, chimneys
Bisphenol A epoxy	1000	135/160	75	3,400	2.6	SMC-/BMC resin with high corrosion resistance; used under the hood

Table 1.6 Properties of various VE resins [11], HDT = heat deflection temperature according to DIN EN ISO 75-1/2. T_g = glass transition temperature, σ_{ts} = tensile strength, E_0 = Young's modulus, ε_B = tensile strain at break

VE resins are utilized in applications with aggressive media, e. g., large glass fiber reinforced pipes for gas ducts in flue gas desulphurizing plants, as well as scrubbers, cooling towers, ovens, piping, and boat construction. Also storage tanks, heat

accumulators, transport containers, and chemical resistant grilles are manufactured from glass fiber reinforced VE resins; sewer cleaning is also a large area of application. Because of their toughness, they are used as compression molded bumper supports. Their high strength predestines them for large supporting applications, such as bridges with pultruded pillars. They are also replacing UP resins in rotor blade construction. Reinforced with fillers, they are used as dowels for connection anchors. The special properties of VE resins are

- Similar to UP resins, but higher in quality (tougher) and more expensive;
- Wide processing variability via choice and quantity of styrene and accelerators;
- Wide range of applications with chemical exposure;
- Environmental impact due to styrene;
- Brand names: Atlac (DSM Composites Resins), Derakane (Nordmann Rassmann GmbH, Ashland).

■ 1.2 General Remarks, Definition of Terms

Modern technology is implemented in ever shorter development times and under stricter legislative regulation. This book was written to help ensure high quality and serviceability in product development.

One of the main advantages of plastics is their varied, but overall remarkable durability in contact with media and in different climates. In machine and plant construction, in building and vehicle construction, and even in medical technology, high-polymeric materials have established themselves in areas of application that continue to widen due to continued further development of such materials. Here, an interesting interaction can be observed between application areas, substitutions, and new solutions based on chemical and physical principles this book will cover for many reasons, not the least of which is to avoid misapplications.

1.2.1 Definition of Aging

By “*aging*” of plastics we mean the entirety of chemical and physical changes to polymer materials over the course of time that lead to the alteration of their mechanical properties to the point where the service life of plastics products is reduced. In a more general sense of the term, the aging of plastics is defined as any change in the molecular, supermolecular, or phase structure of polymer materials that leads to changes in their physicochemical properties during manufacture, processing, storage, or service.

According to DIN 50035, aging in polymers can be generally defined – both negatively and positively – as any irreversible change in the property profile the affected material may experience in the course of time for any number of reasons [12].

All processes that take place in a component part are the result of internal or external *causes of aging*.

Internal causes of aging can be thermodynamically unstable states in the material, which initiate processes leading to measurable changes in properties, typically by thermal activation. Examples of such causes are incomplete polycondensation, unstable crystallization states, incompatibility of polymer/plasticizer systems (miscibility gaps), residual stresses due to inhomogeneous density distribution, and orientation stress. Often the heat content in the material at room temperature is sufficient to initiate processes at a notable rate, so that purely time-dependent aging without external influences is at work, even though these cases should be labeled thermal aging. Storage at elevated temperature would not in itself be the cause of aging, but only an accelerating factor [13].

External causes of aging that alter stable materials under normal environmental conditions are more important than inherent material- and process-dependent causes of aging. Here we consider chemical and physical influences of the surroundings on the material: load due to weathering, ionizing radiation, temperature, chemical and biological media. Under most operating conditions, the material's surface is in contact with atmospheric oxygen and moisture. The effect of elevated temperature and UV light make the reaction with oxygen a more or less dominant part of the aging process, depending on conditions [13].

According to the German DIN 50035 [12] we distinguish between chemical and physical aging processes, although in practice they often take place simultaneously.

Chemical aging processes are processes during which changes take place in the chemical composition, molecular structure and/or molecular weight of the material or, in multi-material systems, in at least one of the materials components. The most important aging processes are: oxidation, degradation, hydrolysis, post-condensation, and post-polymerization. Chemical aging processes are irreversible, i. e., changes in the material are preserved after remelting.

Physical aging processes are processes that involve changes in the structure, the molecular state of order, the ratio of component concentration (in multi-material systems), and/or the external shape and structure or measurable physical properties as long as it does not lead to chemical degradation. The most important phenomena of physical aging are relaxation, post-crystallization, separation, plasticizer migration, agglomeration (e. g., blooming, exudation). Physical aging processes are reversible, i. e., changes are no longer present after melting.

At this point it should be noted that the aging phenomena of plastics have yet to be explained entirely. There are various reasons for this problem. To begin with,

the aging behavior of plastics is very complex. Various reactions take place simultaneously, so that the results of many investigations reflect overlapping reactions. Second, degradation is influenced by contamination and degradation products formed during processing. Moreover, isolating primary degradation products is often problematic, so that primary and secondary reaction products are superimposing. The interaction between these factors remains unknown. And finally, reactions in the solid state are superimposed by geometric influences, crystallinity/morphology, orientation, processing methods (formation of orientations and sink holes), moisture absorption, permeability, and diffusion processes [14].

1.2.2 Additional Concepts

The concept of *chemical resistance* in plastics characterizes the resistance of that plastic material to aggressive media, radiation, and long-term mechanical loads. However, the concept of chemical resistance often raises objections. It has been proposed to use the neutral term “*behavior toward ...*” instead. However, the term chemical resistance is wide-spread and in constant general use, although it lacks univocal conceptual content, since the demands made on plastics differ from one case to another. Thus the concept of chemical resistance should not be applied to a material itself, but to finished parts made from polymers, having a particular intended use, such as polypropylene piping for waste-water from buildings [13].

By *service life* we mean the intended length of time for a component part to be used under operating loads, i. e., the entirety of forces, moments, stresses, strains (distortions), deformations, temperatures, media, and radiations affecting a component part.

Durability describes the capability of a technical system to retain its properties to the extent necessary during its required service life.

Fatigue is a collective concept for processes that take place (especially in metallic materials) under repeated, cyclic mechanical and/or thermal loading which typically impair the functionality of the component part as loading proceeds. In plastics, the concept of fatigue involves the aging effects of dynamic loads, such as crack formation and propagation as well as the associated fatigue structures.

Life span is the time during which the component part is fully functional, i. e., is capable of absorbing operating loads, creep loads, stress cycles, temperature cycles, etc. (see service life). Life span should always be longer than service life and aims at longevity.

Product safety – product liability link technology and regulatory environment for all products both on the market and under development. This involves the proven safety required by regulation regarding the safety for products and equipment,

ensuring the elimination of damage/accidents, i.e., dangers to the health or safety of persons.

The *safety* of parts is rated higher than materials-related natural and technical risks. Safety strategies range from practical service life/life span calculations to statements regarding the durability/rating of plastics parts based on probability calculations (probabilistics).

Damage is a negative impairment of loadability or another aspect under consideration (e.g., deformations, micro-cracks) up to an admissible level and depends on the functionality of the part. This admissible level of damage must not be exceeded. The damage process generally begins during processing and assembly and, therefore, has to be limited and/or considered for the remaining service life.

Reliability is the capability of an aspect under consideration to fulfill its function under specified conditions during a specified time. Here, survival probability plus failure probability are unity, i.e., the highest probability of survival is achieved at a failure probability approaching zero.

■ 1.3 Short and Long-Term Behavior

The behavior of component parts under short-term temperature effects depends on both product specific thermal properties and the duration and type of the temperature effect as well as on loading. The design and processing of the component part are also decisive.

The short-term behavior of plastics under thermal loading is determined by their softening behavior and physical aging processes, whereas long-term behavior is mainly dominated by chemical degradation.

1.3.1 Softening Behavior

Softening behavior plays a decisive role mainly under high thermal loads (such as when plastics substrates are welded) and is determined by the glass transition temperature in amorphous and by the melting temperature in semi-crystalline plastics, see Section 5.4.4.

The softening behavior is characterized by the heat distortion temperature. This is the temperature at which a test specimen deforms up to a limit value under a particular external load [15]. The determination of heat distortion temperatures is performed according to various processes such as Vicat (ISO 306 [16]) or ISO 75 [17]. These processes involve one-point, fast determination methods. The various

processes are used to determine strongly deviating heat distortion temperatures, depending on load and the defined final criteria [15]. However, there is no systematic relationship between these measured values. This is due to the fact that stresses, as well as the limit values of deformation, vary depending on the method used. Heat distortion temperature also depends on crystalline structure, orientations, residual stresses as well as the thermal expansion behavior.

1.3.2 Aging Behavior

Once in use, plastics are subject to different service conditions while two aging processes take place simultaneously, Figure 1.4:

- In physical aging processes, a morphological change occurs. This process is reversible via melting.
- In chemical aging processes (chemical degradation), the macromolecules are degraded either beginning at the surface of the finished part (e.g., diffusion controlled oxidation or weathering) or homogeneously (e.g., through hydrolysis). This process is not reversible via melting [18].

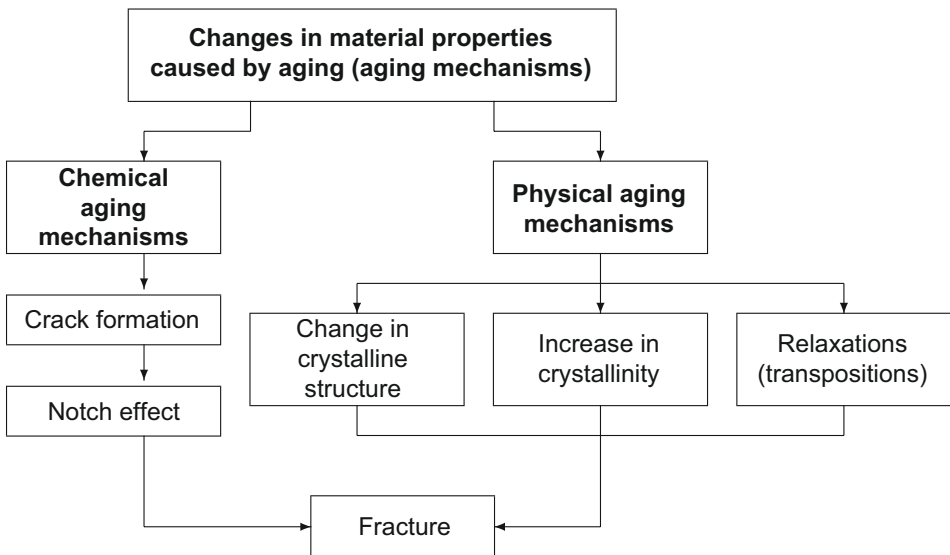


Figure 1.4 Simplified diagram of aging processes [18]

Physical aging processes are changes in the physical structure of plastics without changes to the molecular chains, Figure 1.5 left, see Section 1.3.4. Chemical degradation, on the other hand, results in changes in the chemical structure of the molecular chains, Figure 1.5 right, see Section 1.3.3 [19].

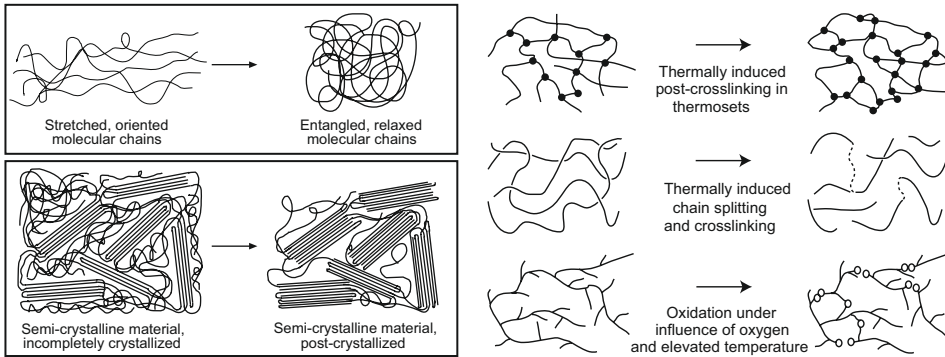


Figure 1.5 Effects of aging [19]

Left: effects of physical aging processes on oriented and semi-crystalline plastics
(top: relaxation processes, bottom: post-crystallization)

Right: chemical aging processes and chemical degradation in plastics

Chemical aging processes represent a change in chemical composition and molecular structure, whereas physical aging processes cause changes in external shape as well as physical structure. It is often impossible to distinguish clearly between the effects of chemical and physical aging processes, because they usually take place simultaneously causing complex effects.

1.3.3 Chemical Aging Processes (Chemical Degradation)

The fundamental weaknesses of plastics are caused by their macromolecular structure and relatively weak bonding forces. Plastics are thus subject to decidedly greater influences by the effects of heat, light, and oxygen, etc. than are metals or mineral materials. These and additional external influences, such as chemicals and radiation, initiate chemical aging processes that cause the deterioration of properties and thus shorten the life span of plastic parts.

Chemical aging processes in polymer materials cause changes on the molecular scale and lead to chain cleavage but also to crosslinking and cyclization. The radicals thus formed (see Figure 1.13) react by isomerization, dimerization, oxidation, or reduction and thus cause a change in chemical composition and molecular structure.

These changes can be essentially classified into three groups:

- *Change in molecular structure:* molecular mass decomposition, change in molecular weight distribution, as well as branching and crosslinking,
- *Formation of functional groups,*
- *Cleavage of low-molecular products:* depolymerization, side-group cleavage.

A change in molecular structure can affect mechanical properties such as tensile and bending strength as well as tensile strain at break, impact strength, and melt flow properties. Figure 1.6 uses PP homopolymers as an example to show that toughness increases with increasing molecular mass. It is apparent that molecular degradation can have particularly strong effects on mechanical properties: Below a critical molecular weight, yield strain and tensile impact strength are drastically reduced.

The formation of functional groups can cause color changes, thus influencing transparency and optical quality. Furthermore, electrical properties may be impaired. Cleavage of low-molecular groups may cause odors and also influence mechanical properties [20].

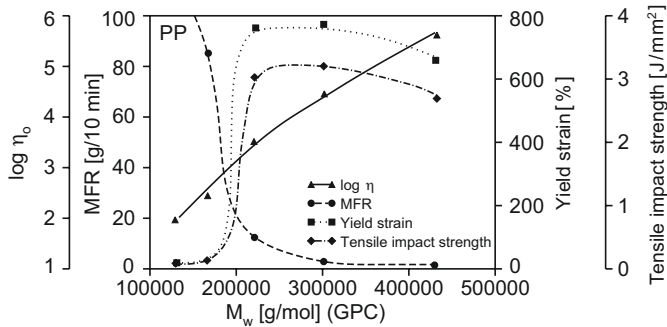


Figure 1.6 Mechanical and rheological properties of a polypropylene homopolymer as a function of molecular weight (at comparable index of dispersion) [21]

Besides mechanical properties, rheological properties are influenced by molecular weight. The zero viscosity follows a power law for many plastics melts, expressed in Eq. 1.1:

$$\eta_0 = K \cdot M_w^{3.4} \quad (1.1)$$

with η_0 = zero viscosity
 K = constant
 M_w = average molecular weight

This means that even small changes in molecular weight caused by damage to the plastic can result in strong changes in viscosity.

1.3.4 Physical Aging Processes and Physical Aging

1.3.4.1 Physical Aging Processes

Physical aging processes are always the result of thermodynamically unstable states (residual stresses, orientation, incomplete crystalline structure) caused by process-dependent cooling conditions during the manufacture of plastic products.

Here, the plastic material solidifies in an undercooled melt so that it is impossible to reach an equilibrium state. Physical aging processes as mentioned in DIN 50035 [12] are relaxation processes of residual stresses and orientations, post-crystallization, separation, agglomeration as well as loss of plasticizer, plasticizer migration, or plasticizer extraction (see Figure 1.5). Physical aging processes are accelerated by elevated temperatures. A change in physical structure caused by physical aging processes is often accompanied by a change in dimensions that creates mechanical stresses in the material due to inhibition of elongation or shrinkage. Cracks or fractures are the result of such stresses.

Physical aging processes also change properties such as water absorption and diffusion and oxygen diffusion. This has consequences for mechanical properties and the progress of chemical degradation processes. Oxygen diffusion decreases as crystallization and orientation increase.

A distinction must be drawn between the concept of “physical aging processes” and the classical concept of “physical aging” (Section 1.3.4.2), although it is not always clearly drawn in practice. The concept of “physical aging” is often used with the material changes defined by DIN 50035 under “physical aging processes”.

1.3.4.1.1 Post-Crystallization

Post-crystallization takes place in semi-crystalline plastics mainly at elevated temperatures. However, it can take place at room temperature, as illustrated by the cold crystallization of rubbers or the post-crystallization of TPU. Post-crystallization involves a change in physical structure, leading to an increase in the degree of crystallization and lamellar thickness, and to a refinement in crystalline structure: At the point of transition between crystalline and amorphous zones, the amorphous molecular chains attach themselves to the higher melting crystallites, Figure 1.5 left. As the molecules become more densely packed, this may result in shrinking and/or warping with crack formation [22].

1.3.4.1.2 Relaxation of Orientations

Flow processes during manufacturing cause the macromolecules and fillers to orient in the direction of flow, especially during the filling phase in injection molding. Simultaneously, entropy elastic restitution causes relaxation processes. Orientation relaxation in solid plastics takes place at elevated temperatures ($T > T_g$) and is always accompanied by shrinkage phenomena, leading to warping and crack formation in the part [23].

1.3.4.1.3 Relief of Residual Stresses

Residual stresses can be defined as local mechanical stresses present anywhere in a molded part in the absence of external forces. Here, the resultant of the forces and moments must be zero [24].

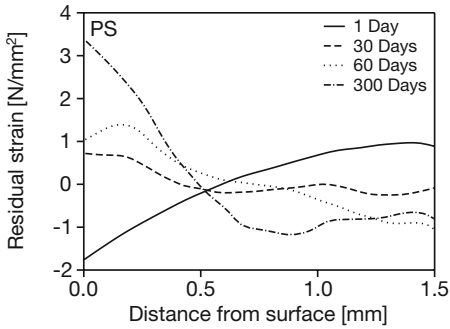


Figure 1.7

Residual stress distribution (detected by removal of layers) in flat shoulder test bars made from polystyrene ($T_m = 200\text{ }^\circ\text{C}$, $T_w = 30\text{ }^\circ\text{C}$) after different aging periods at $23\text{ }^\circ\text{C}$ [24]

Residual stress in both amorphous and semi-crystalline plastics are mainly the result of non-uniform changes in molded part volume caused by temperature gradients as the molded part cools down from temperatures above its glass transition temperature.

The temperature gradient depends on the type of plastic, on the geometrical shape of the part, and processing conditions [24]. However, residual stresses can also develop due to plasticizer migration. Relaxation of residual stresses can lead to shrinking and warping [23].

Figure 1.7 uses polystyrene to illustrate the influence of storage time on residual stresses, both quantitatively and qualitatively. At the surface, 30 days of storage suffice to turn compression stress into tensile stress. The quantitative increase is considerable; the stresses in the surface layers increase five-fold between storage times of 30 and 300 days. A neutral stress zone can be found at a depth of 0.4 and 0.7 mm measured from the surface. The tensile stress turned into compression stress in the center of the specimen [24].

If the components have different softening temperatures (and thus different thermal coefficients of expansion), (thermal) residual stresses also build up in polymer blends as the melt cools. Examples include the classic rubber-modified, impact resistant polymer systems (e.g., HI-PS, ABS, ACS) in which considerable residual stresses (shrinking stresses) build up in the rubber particles during cooling from the melt. These stresses generate hydrostatic tensile stresses within the particles and radial tensile stresses at the surface (particle/matrix-border layers). The glass transition temperature of the rubber phase is thereby lowered, and craze formation (that leads to increased impact toughness) is modified. Relief of these residual stresses thus influences the resulting mechanical behavior [25].

1.3.4.2 Physical Aging

The classical concept of “physical aging” describes property changes in plastics resulting from the thermodynamic imbalance in the amorphous phases present below the glass transition temperature [26], [27].

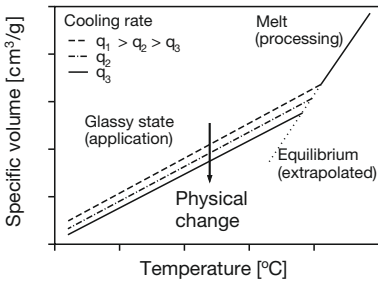


Figure 1.8
Schematic illustration of the dependence of specific volume on temperature [28]

Figure 1.8 provides a schematic illustration of the specific volume profile as a function of temperature [28]. The reason for the dependence of specific solid-state volume on cooling rate is the dependence of molecular motion on both temperature and free available volume. At elevated temperatures, sufficient free volume and enough thermal energy are present to facilitate transposition processes. Therefore, the polymer molecules can assume their thermodynamic state of equilibrium. With decreasing temperature, free volume decreases at a higher rate than thermal excitation. With decreasing free volume, molecular motion decreases simultaneously and, coupled with it, the rate at which free volume can change. When the temperature falls below glass transition, there may still be enough thermal energy present, but the limited amount of free volume restricts molecular motion. The available free volume is frozen at a value higher than the value of thermodynamic equilibrium. The plastic will continue to assume its state of equilibrium (although with a significant time lag) because of the thermodynamic momentum still present [28].

Often, the concept of “physical aging” is not used in this strictly limited sense, but rather generally, describing changes in physical structure that occur during the life span of plastics materials.

■ 1.4 Influencing Factors

The aging of plastics is influenced by external and internal factors:

- External factors
 - Temperature
 - Oxygen concentration
 - Atmospheric loads
 - UV light
 - Humidity

- Environmental media
- Contaminations
- Radiation
 - Wave length
 - Intensity
 - Type of radiation
- Mechanical loads
- Biological loads (macro- and microbiological)
- Internal factors
 - Chemical structure
 - Chain structure
 - Molecular weight and weight distribution
 - Structure of the molecular chains
 - Radical concentration
 - Physical structure
 - Crystallite structure
 - Crystallinity
 - Morphology
 - Free volume
 - Orientations
 - Residual stresses
 - Others
 - Contamination
 - Stabilizers
 - Remaining catalyst

The final properties of every polymeric material are determined by its chemical composition and its physical structure. Whereas chemical composition mainly affects its chemical aging processes, physical structure affects both chemical and physical aging processes. Other factors, such as catalytically active contamination, can affect all aging processes. Chemical and physical aging processes also influence each other, e.g., post-crystallization can reduce oxygen diffusion and thus affect oxidation and vice versa [19].

1.4.1 Effect of Temperature

1.4.1.1 Accelerative Effect of Temperature

Besides direct physical and chemical effects, temperature plays an important role in all chemical reactions, because temperature increases lead to accelerated chemical reactions.

For the simplest case of a monomolecular reaction, the reaction rate, i. e., the temporal change in concentration c_A of material A is proportional to the momentary concentration of A :

$$-dc_A / dt = k \cdot c_A \quad (1.2)$$

with k = reaction rate invariable
 c_A = concentration of A

The reaction rate invariable k increases exponentially with temperature according to *Arrhenius* (see Sections 1.6.2.4 and 2.1.1). This exponential dependence corresponds to *Van't Hoff's* empirical "reaction rate-temperature rule" which states that a temperature increase of 10 °C causes a two- to threefold increase in reaction rate [29]:

$$k = \alpha \cdot e^{-\frac{E}{RT}} \quad (1.3)$$

with E = activation energy as energy threshold
 R = general gas constant
 α = no. of impacts, frequency of possible molecular transformations

The concentration c_A of chemical components is assigned a particular property P , e. g., tensile strength.

$$P = F(c_A) \text{ and } c_A = f(P) \quad (1.4)$$

Combining the equations and subsequent integration, results in:

$$t = \left(\frac{1}{\alpha}\right) \cdot \ln \left[\frac{f(P_0)}{f(P)} \right] \cdot e^{\frac{E}{RT}} \quad (1.5)$$

with P_0 = P for $t = 0$
 P = property

If P_z is the value at which the material has reached a specified property limit, a life expectancy t^* then results as:

$$t^* = \left(\frac{1}{\alpha}\right) \cdot \ln \left[\frac{f(P_0)}{f(P)} \right] \cdot e^{\frac{E}{RT}} \quad (1.6)$$

with t^* = life expectancy

The life span-temperature characteristic profile can be graphically represented as a straight line, Figure 1.9, where the time in logarithmic scale is the ordinate and the reciprocal value of absolute temperature is the abscissa. The result is parallel arrays of curves for different amounts of a property change, represented as quotient P_0/P , or for the same degrees of change of different properties.

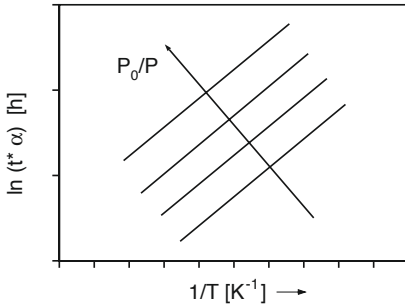


Figure 1.9
Profiles of various degrees of change [29]

In contrast to these simplifying assumptions, several chemical reactions are simultaneously involved in plastics degradation processes. Nonetheless, the usefulness of these life span estimations has proven to be a valid basis for investigations of plastic aging. This is due to the fact that, even in complicated chemical reactions, a particular partial process is decisive for the progress of the entire reaction and thus for the reaction rate [29]. Once in service, molded plastic parts are not always subject to uniform temperature distribution, but to variations in the load collective. The simplest approach to solving this problem is to assume “damage accumulation” according to the *Miner rule*:

$$\sum_i \frac{t_{xi}}{\tau_{xi}} = 1 \quad (1.7)$$

with t_{xi} = time under defined static conditions
 τ_{xi} = life span corresponding to t_{xi}

In the simplest case of aging at two different temperatures T_1 and T_2 , Eq. 1.7 becomes:

$$\frac{t_{x1}}{\tau_{x1}} + \frac{t_{x2}}{\tau_{x2}} = 1 \quad (1.8)$$

with t_{x1}, t_{x2} = exposure time at temperature T_1 or T_2 , respectively
 τ_{x1}, τ_{x2} = life spans corresponding to t_{x1} and t_{x2}

It follows that:

$$t_{x1} = \tau_{x1} - a_{12} t_{x2} \quad (1.9)$$

whereby

$$a_{12} = \frac{\tau_{x1}}{\tau_{x2}} \quad (1.10)$$

with a_{12} = shift factor

This is the case only if the time-temperature shift (see Section 1.6.2.5) is fulfilled, which is symbolized by an Arrhenius-like relation for the shift factor:

$$a = e^{\left[\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]} \quad (1.11)$$

with a = shift factor

T = temperature

T_{ref} = reference temperature

If Eq. 1.10 is not valid, the assumption of damage accumulation according to Eq. 1.8 is also no longer valid. Equation 1.8 then shifts to a non-linear relation of the type

$$\frac{t}{\tau_{x1}} = 1 - g\left(\frac{t}{\tau_{x2}}\right) \frac{t}{\tau_{x2}} \quad (1.12)$$

Where function g has to be determined experimentally.

“Damage accumulation” according to the Miner-rule often does not fail because the invalidity of the relation, but due to the fact that the temperature-time collectives of the component are not known. Long-term measurements are often required to determine these values. Such long-term measurements are published in reference [30] for component parts made from ABS in a highly thermally loaded zone of an instrument panel.

1.4.1.2 Chemical Degradation

1.4.1.2.1 Thermal Degradation

Cleavage of chemical bonds in the polymer backbone is an axiomatic characteristic of thermal degradation in plastics. The result is a reduction in molecular weight and the potential formation of volatile low-molecular degradation by-products. Chain cleavage of linear polymers may lead to crosslinking or cyclization; here, the former causes an increase in molecular weight. Cause for thermally induced chain cleavage is the overstraining of intramolecular bonds. With increasing temperature, these bonds are increasingly loaded by oscillating atoms until bond cleavage occurs. The thermally activated bond cleavages are statistically distributed so that hydrogen or methyl group cleavage can take place in addition to chain cleavage. The radicals formed by cleavage represent the starting points for further oxidative degradation reactions.

Purely thermal degradation takes place when, typically at higher temperatures, the plastic degrades without the involvement of another component (pyrolysis). The pyrolytic reaction sequence (without superposing oxidative degradation) can only take place under total exclusion of oxygen in inert and dry atmosphere. In practice, however, this superposition of oxidative and/or hydrolytic degradation typically takes place.

Among the strictly thermally induced types of degradation we distinguish between:

- Statistical chain splitting with reduction in molecular weight without the formation of low-molecular compounds,
- Depolymerization with monomer formation without a significant change in molecular weight (e.g., PMMA, PS, POM),
- Elimination with side group cleavage and formation of low-molecular compounds (e.g., PVC with HCl formation).

The reactions can overlap, depending on the polymer and temperature. Figure 1.10 shows the average degree of polymerization as a function of weight loss for depolymerization, statistical chain cleavage, and the superposition of both mechanisms, respectively. For pure depolymerization (“zipper mechanism”), the average degree of polymerization, and with it the molecular weight of the plastic material, decreases only slowly with the weight loss. Here, degradation usually begins at the chain end [20].

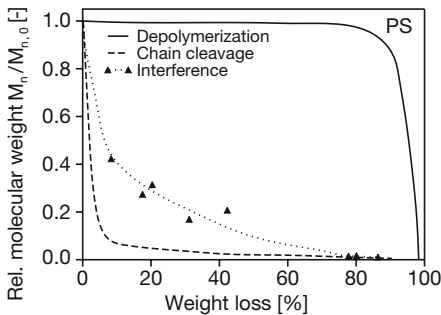


Figure 1.10
Relative molecular weight as a function of weight loss in polystyrene [20]

The progress of thermal degradation in plastics depends on their chemical composition and temperature. The degree of thermal degradation increases with increasing temperature. Molecular weight may actually increase due to crosslinking.

Table 1.7 shows the bond energies of chemical bonds. These bond energies were determined in investigations of small molecules. Intermolecular forces in plastic materials may in some cases impair the bond energies [31].

Bond	Bond energy (kJ/mol)	Wavelength (nm)
C \equiv N (nitrile)	875	136.8
C \equiv C	836	
C = C	837	142.9
C = O (ketone)	729	164.3
C = C (H-C=C-H)	838	
C = C	607	
C = C (H ₂ C=CH ₂)	524	
C = S	540	
C - C (aromatic)	519	230.6
C - H (acetylene)	506	236.3
C - F	498	240.3
C - F (sec. C atom)	389	
O - H	460	260.0
C - H (ethylene)	444	269.7
C - H (methane)	443	
C - H (prim. aliphates)	411 - 427	
C - H (sec. aliphates)	394	
C - H (tert. aliphates)	373	
Si - O	373	
C - O	364	328.6
S - H	364	
N - H	352	340.4
C - C (F ₃ C-CF ₃)	406	
C - C (C ₆ H ₅ -CH ₃)	373	
C - C (aliphatic)	335	357.4
C - O (sec. C atom)	443	
C - O (ether)	331	361.9
C - Cl (tert. C atom)	327	
S = S	317	
C - Cl (C ₆ H ₅ CH ₂ -Cl)	317	
Si - H	314	
Si - C	293	
C - N (nitromethane)	285	
C - S	276	
O - O (peroxide)	268	446.7
C - N (amide)	222	539.5
N - N (hydrazine)	155	

Table 1.7 Bond energy of primary valence bonds with corresponding light wavelengths [20, 31, 32, 33]

The amount of bonding energies indicates that up to a temperature range of 250 to 300 °C, thermal degradation is usually not to be expected (see Figure 1.11 and Section 5.4.2.1.1). At higher temperatures, however, such as during processing, thermally induced chain cleavage can occur.

1.4.1.2.1.1 Depolymerization

Depolymerization trends are illustrated in Table 1.8. The side groups on the α -carbon atom are decisive for the tendency of plastics to depolymerize. Thus, polystyrene depolymerization increases significantly when a methyl group (poly- α -methylstyrene) is present at the α -C atom instead of a hydrogen atom. During depolymerization, monomer cleavage may cause strong odors [20].

Polymer	Monomer content (mol %)
Poly- α -methylstyrene	100
Polyoxymethylene	100
Polytetrafluoroethylene	96
Polymethyl methacrylate	95
Polystyrene	41
Polyisobutene	20
Polybutadiene	20
Polyisoprene	11
Polyethylene oxide	4
Polymethylacrylate	1
Polyethylene	1
Polyacrylonitrile	0
Polypropylene	0
Polyvinyl chloride	0
Polyvinyl alcohol	0

Table 1.8

Thermally induced formation of monomers (during thermal degradation in inert atmosphere) as an indicator for depolymerization during pyrolysis of various polymers in air (see Table 5.38) [20]

1.4.1.2.1.2 Chain Cleavage

In many macromolecular systems, chain cleavage does not take place uniformly, but depends on the position in the chain and the chain length [34]. The valence bond can be cleaved either in the backbone or in a side chain. Because in many cases the bond energy between the C-C bonds in the backbone is weaker than the bond energy between the backbone and a side group, the bond energies of the backbone determine thermal stability [20].

Chain cleavage within a polymer chain preferably takes place at weak bonds (“weak links”) present in statistical distribution over the entire molecule. As a result of chain cleavage, molecular weight is significantly reduced, and cleavage of volatile components is minimal, Figure 1.10 [20].

Figure 1.11 depicts this relationship between backbone bond energy and decomposition temperature. A small increase of 20 kJ/mol in bond energy leads to an increase in decomposition temperature of more than 30 °C. Figure 1.11 also shows that the weak bonds in the backbone are prone to thermally induced cleavage [20]. Thermal degradation is significant only at higher temperatures. This is due to the high activation energy for thermally activated chain cleavage. The thermal chain cleavage of polyethylene exhibits an activation energy of 264 kJ/mol (whereas oxidative degradation requires only 96 kJ/mol) [20].

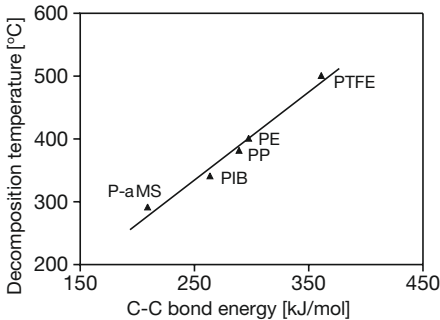


Figure 1.11
Relationship between backbone bond energy and decomposition temperature (temperature at which half of the polymeric material has become gaseous after 30 minutes) [20]

In addition to backbone bonds, the chemical structure of side groups and irregularities in the molecular structure play a role. Side group cleavage can take place prior to backbone cleavage, e. g., in PVC [20].

1.4.1.2.1.3 Side Group Cleavage

Side groups are cleaved preferably when the bond energy between the C atoms in the backbone and the side group is weaker than that of the C-C bonds in the backbone, see Table 1.7. Bond energy depends not only on the atoms bound by the valence bonds, but also on molecular constitution, i. e., on the chemical environment of the bond [20].

1.4.1.2.1.4 Crosslinking

Polyethylene tends to crosslink at low processing temperatures, but at increased temperatures it tends to degrade due to chain cleavage, because the activation energy required to crosslink PE is 96 kJ/mol, while 264 kJ/mol are required for chain cleavage caused by elevated temperature. Crosslinking will thus occur at lower temperatures, chain cleavage at higher temperatures. Crosslinking is caused by dimerization of various macro-radicals, see Figure 4.42.

1.4.1.2.2 Thermal-Oxidative Degradation

Thermal-oxidative degradation takes place in the presence of oxygen (see Section 1.4.2). It begins at temperatures lower than strictly thermal degradation in inert atmosphere. Here, the composition of the polymer material changes as oxidation products are formed, see Figure 5.157.

1.4.1.2.3 Thermal-Mechanical Degradation

1.4.1.2.3.1 Thermal-Mechanical Degradation in Polymer Melts

Mechanical degradation is defined as chain cleavage caused by external mechanical load (e.g., strain). According to one theory, molecular load is highest in the chain center, resulting from the impairment of molecular rotations and from the shear and tensile stresses dominant in flowing melts. The molecular load increases with longer molecule chains and higher shear stresses. Thus, breaks occur mainly in the center of the molecular chain. Other approaches assume that the damage already occurs in the feed section of a screw caused by the frictional energy exerted [35]. The reactive primary radicals resulting from mechanical degradation continue to react according to the radical chain reaction shown in Figure 1.13.

1.4.1.2.3.2 Stresses Caused by Temperature Gradients

Temperature gradients cause stresses in molded parts made from polymers. Because the equation for heat conduction and the diffusion equation are identical, the same statements are valid as for water diffusion, see Section 1.4.3.2. But because temperature conductivity is higher than the diffusion coefficient, all temperature equilibrating processes proceed much faster and the accompanying mechanical stresses act for a shorter time [36].

In (double and multiple) glazings and covers, for example, temperature gradients create mechanical stresses proceeding from the center to the surface if geometry or design prevent the molded plastics part from relaxation by deformation [36].

1.4.1.2.4 Ablation

Ablation is the removal of material caused by melting and evaporating. Contrary to general perception, plastics are subject to very little ablation, because they can absorb, dissipate, and store heat – although that involves changes in the material. This property is decisive for their application in heat shields designed for space craft. Polytetrafluoroethene is used for such heat shields, as well as SiO₂-filled phenolic resins or epoxy resin/polyamide combinations filled with SiO₂ and polyimides, silicones, phosphonitrilic chlorides, and polyboron phosphorous compounds.

As heat is introduced to the material, it is absorbed and conducted further internally. Because plastics typically exhibit poor heat conductivity, the temperature rises. At this stage, water, residual solvent, and oligomers evaporate, dissipating the enthalpy of evaporation. At even higher temperatures, side group cleavage

begins, possibly also backbone cleavage and irreversible pyrolysis and reversible depolymerization compete with each other. If pyrolysis becomes dominant, carbon is created. Carbon introduces good heat protection owing to its endothermic creation as well as to its high heat capacity and good heat radiation. However, the plastic can also begin to soften and then evaporate, always under absorption of heat.

1.4.1.3 Physical Aging Processes

Any temperature increase in plastics causes an increase in molecular motion. Below the glass transition temperatures, usually only vibratory and rotary motions of individual side groups are possible. However, backbone motion can take place to some extent, such as secondary relaxation in polycarbonate. In the glass transition range, chain segments may rearrange or rotate. To enable these rearrangements, there must be sufficient free volume in the plastic. The amount and size of free volume increase with increasing temperature [1]. Translational motion of the molecule becomes possible only above flow temperature.

Temperature thus influences physical aging processes by increasing both the mobility of the molecular chains and the free volume. Both factors promote relaxation or post-crystallization.

1.4.2 Effects of Oxygen

Oxidation in plastics is influenced by

- Oxidants
 - Oxygen, air
 - Ozone
 - Nitrogen oxides
- Loads
 - Thermal
 - Electrical
 - Mechanical
 - Radiation
- Catalysts (external)
 - Copper and/or brass connectors or sheathing (esp. for polyolefins)
 - Iron (additives)

Oxidation in plastics affects both their molecular structure (chemical structure) and their micro-structure (physical structure, morphology) [37]. Figure 1.12 shows the influences of thermal-oxidative processes, UV aging, and thermal-mechanical load on a non-stabilized polypropylene during processing [38].

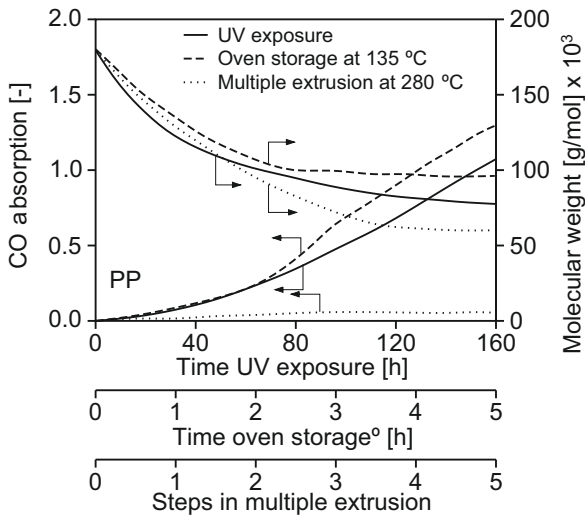


Figure 1.12
Carbonyl absorption, change in molecular weight of polypropylene after multiple processing, oven aging, and UV loading [38]

1.4.2.1 Chemical Degradation

Three mechanisms describe the oxidative degradation of plastics, and although they may act simultaneously, usually one of the mechanisms is dominant:

- Chain cleavages
- Chain crosslinking
- Chain branching

Which reaction is dominant depends on the physical condition and chemical structure of the plastic (see Section 1.4.5.1), the reaction partner (oxygen, ozone), and the loads experienced [37].

Plastics containing mainly saturated macromolecules oxidize in a similar mechanism as low-molecular hydrocarbons. Here, a radical chain reaction with three elementary reactions takes place, Figure 1.13 [34]:

- Initiating reactions,
- Degradation by chain-propagation and branching and
- Termination reactions.

Free radicals cause the initiation reaction, Figure 1.13. These alkyl radicals are formed by thermal energy, radiation, mechanical load during processing, or under the influence of metal ions.

The high bond energy of saturated hydrocarbons (see Table 1.7) prevents bond cleavage until very high temperatures are reached [42]. By contrast, bonds in peroxides and aliphatic azocompounds with dissociation energies of 130 to 170 kJ/mol are cleaved at temperatures of 70 to 150 °C. Generally speaking, the dissociation energy is the lower the more stable the created radicals are [42].

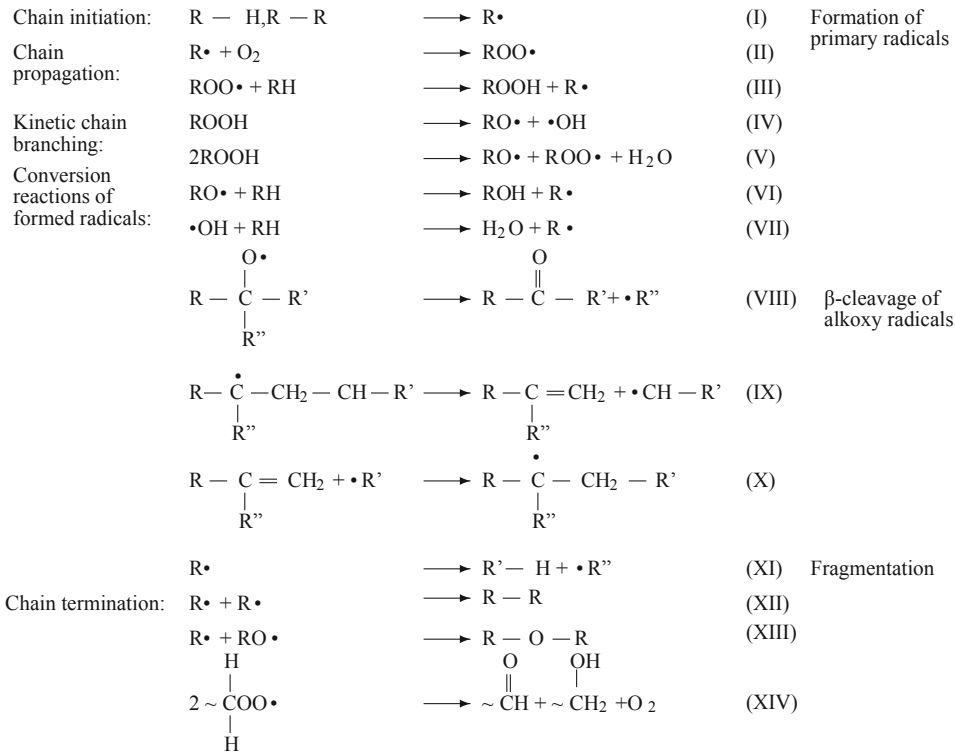


Figure 1.13 Schematic of radical chain reaction during oxidation of plastics [38, 39, 40, 41]

Small amounts of peroxides or other oxygen-containing components or contaminations may also initiate the formation of radicals. Oxygen accumulates at the free bond of the macro-radical – practically without activation energy – creating reactive macro-alkylperoxyl radicals (II). They react with a second polymer molecule forming a hydrogen peroxide (III). The activation energy for this reaction is high, and under processing conditions these hydrogen peroxides have a life span of several ten seconds, so that this reaction is rate-determinant. Because of the low stability of the O-O-bonds, the hydrogen peroxides degrade under formation of alkoxy radicals (IV), facilitating a branching of the chain reaction and proliferation of radicals. The alkoxy radicals can attack the hydrogen atoms in the backbone (VI) and thus propagate the chain reaction or degrade under formation of carbonyl compounds (VIII). The alkyl radicals forming in reactions (VI) and (VII) can degrade under formation of double bonds (IX) that tend toward further reactions (X). Oxidation processes thus accelerated are terminated by the recombination or disproportioning of reactive radicals (VII, VIII), by the formation of less reactive alcohol or ketone compounds (XIV), or by reaction with contaminants. Hydrogen peroxide degradation (V) and β -cleavage of alkyl and alkoxy radicals is responsible for the decrease in molecular weight. The recombination of two macro-radicals

(XII) can lead to crosslinking. The major degradation products are alcohols, esters, carbon acids, and chains with carboxyl groups.

Radical chain reactions are slow at initiation (induction time) and become faster due to the increase in hydrogen peroxides and their degradation to radicals, Figure 1.14. The formation and degradation of hydrogen peroxides are key reactions for all degradation reactions [43], [44], [45]. Degradation rates increase with increasing number of radicals in the cycle. The cycle of oxidative degradation proceeds autocatalytically and is thus called *autoxidation*. It proceeds more or less the same way in all plastics. When describing polymer oxidation by the reaction schematic shown in Figure 1.13, it should be kept in mind that this is a model and that the limited mobility of the macro-radicals and peroxides in the solid phase results in a heterogeneous oxidation process [43].

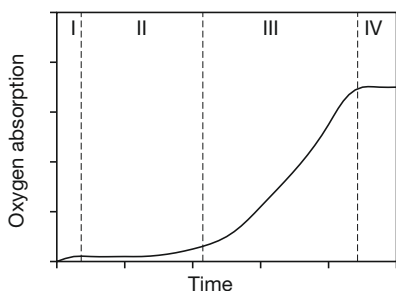


Figure 1.14
Kinetic progress of an oxidation reaction [46, 47]

In the case of saturated hydrocarbons, the start reaction is extremely slow, as long as the reaction takes place at room temperature. Although the precise radical chain reaction has not been entirely determined, it is generally believed that the decomposition of peroxides formed in the polymer during manufacture, modification, and processing represents the main source of the radicals that initiate oxidation [21]. The source of the primary radical $R\cdot$ is still controversial: The direct reaction of oxygen with plastics is ruled out, based on kinetic and thermodynamic considerations. According to one explanation, small amounts of oxygen react with the polymer during polymerization due to the presence of metal ions (as catalysts) and contaminations, thus forming the primary radical. Another hypothesis claims that the radical $R\cdot$ is formed by UV light or by thermo-mechanical load during processing, or as the result of reactions with radicals from a foreign source [48].

The kinetic progress of oxidation has four stages, Figure 1.14:

1. Fast initiating addition of oxygen at active centers,
2. Induction period (dependent on the presence of stabilizers),
3. Increase in oxidation rate caused by radical chain reactions with degenerated chain branches,
4. Reduction of oxidation rate due to reduction of reactive centers.

Oxidation does not proceed homogeneously in solid plastics: Due to the structure and morphology of the material, contaminations, catalyst residues, and cage recombinations of radicals, active centers (mini-reactors) can form in the plastic [49] from which oxidation spreads out over the entire material.

It has been shown for non-stabilized polypropylene that oxidation takes place heterogeneously and spreads out beginning at easily oxidizable weak spots in the polymer, Figure 1.15.

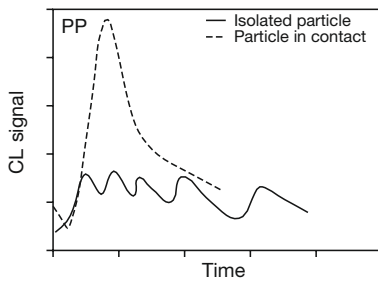


Figure 1.15

Diagram of the chemiluminescence curve for the oxidation of five isolated polypropylene particles (330 μm) compared to polypropylene particles in contact with each other [50]

The isolated polypropylene particles produce a chemiluminescence curve with five peaks that are assigned to individual particles. When the particles are in direct contact, the result is a curve with a single peak that, in its induction time, corresponds to the weakest previously found particle.

This heterogeneous behavior is hard to describe using only the homogeneous process of autoxidation.

In semi-crystalline materials, the heterogeneous character of oxidation can be described by preferential oxidation of the amorphous regions with subsequent oxidative degradation of the crystalline regions.

1.4.2.1.1 Oxygen Absorption

Non-stabilized plastics absorb oxygen relatively rapidly in the beginning phase of oxidation. This is followed by a stationary state with slower oxygen absorption [51]. Both induction time and rate of oxygen absorption increase with temperature and oxygen partial pressure [42].

Induction time depends on the type of polymer (molecular structure, morphology), Table 1.9, while the rate of oxygen absorption is proportional to the mass of the polymer and not to its surface. It decreases with increasing film thickness [52].

	Induction time (h)	
	at 80 °C	at 110 °C
Polyethylene	70	1300
Polypropylene, atactic	4.5	95
Polypropylene, isotactic	7.5	130

Table 1.9

Influence of molecular structure on induction time during oxygen absorption in non-stabilized plastics [42]

1.4.2.1.2 Presence of Metals and Metal Ions

Traces of free metals and metal ions present in polymers have a strong catalyzing effect on oxidation (Figure 1.16), because they are capable of degrading hydrogen peroxides and forming free radicals [53]. On the other hand, they can also stabilize by capturing radicals or degrading radicals into non-radical species [54]. Which of these antagonistic effects is dominant depends on the concentration and oxidation condition [42] of the catalyst residue.

Hydrogen peroxide degradation corresponding to reaction (V) (Figure 1.13) is normally a monomolecular reaction. Metals with 1 electron transfer, i.e., those in which the degree of ionization can shift by ± 1 due to release/absorption of one electron, catalyze the degradation of hydrogen peroxides. In Eq. 1.13, the metal ions act as oxidation agents, in Eq. 1.14 they act as reduction agents.



with M = metal ion
 n = charge no.

The activation energy in Eqs. 1.13 and 1.14 is lower than the activation energy of monomolecular degradation of hydrogen peroxides. Thus the oxidation of plastics is accelerated by the presence of metal ions. Relevant metal ions include iron (Fe^{2+}/Fe^{3+}), cobalt (Co^{2+}/Co^{3+}), copper (Cu^+/Cu^{2+}), chromium (Cr^{2+}/Cr^{3+}), manganese ($Mn^{2+}/Mn^{3+}/Mn^{4+}$), and others.

A dualistic effect on thermal-oxidative stability has been found for copper, cobalt, manganese, titanium, and iron [55].

For example, copper has a promoting effect on the oxidation of polyolefins, see Table 1.10. This is a most unfortunate circumstance, in particular for cable sheathings, because many cables coated in polyolefins are made from copper [56].

PE-HD	Time (h) until embrittlement	
	Brass fitting	PVDF fitting
PE-HD 1	6106	12249
PE-HD 2	7419	10065
PE-HD 3	3753	6108

Table 1.10

Influence of fitting material on the long-term behavior of three different PE-HD grades determined by creep tests [57]

Besides polyolefins, metals also accelerate degradation in natural and synthetic rubbers – an effect called “rubber poison”. Here, mainly copper and manganese are involved, but iron, cobalt and nickel exhibit this effect to a lesser degree [58].

Copper ions exhibit a stabilizing effect on polyamides – in contrast to polyolefins. However, iron and iron compounds have an oxidation promoting effect, Figure 1.16.

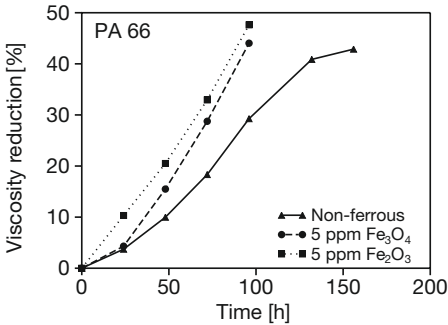


Figure 1.16
Influence of iron oxide traces on the aging behavior of polyamide 66 [60]

In phenolic resins, metals such as copper and iron can promote degradation at concentrations higher than 5 vol.% [59].

In polyethylene, we find increasing promotion of oxidation by various metals in the following order [61]: Cu > Fe > Zn > Pb > Mo > Ti >> Al. In PE-HD manufactured with Ziegler-Natta catalysts, residues in concentrations as low as 1 ppm can lead to considerable deterioration in oxidative stability [55].

The following order of decreasing catalytic effect was found for oxygen absorption in powdered polypropylene: Co > Mn > Cr > Fe > Cu > V > Ni > Ti > Al > Mg > Ba [42]. Even 0.2 to 4 ppm Ti residue from Ziegler-Natta catalysts leads to accelerated oxidation of polypropylene. Higher concentrations cause faster degradation [62].

1.4.2.2 Physical Aging Processes – Chemo-Crystallization

Oxygen affects the physical aging processes of plastics by oxidation and the corresponding increase in chain motion due to chain cleavage, Figure 1.17. This short-chain crystallization, also called “chemo-crystallization”, is caused by chain segments formed by chain cleavage along the surface layer of the lamellae. These chain segments accumulate on the lamellar structure. This “chemo-crystallization” takes place preferably under increased molecular motion, i.e., above the glass transition temperature [19], [63], [64].

Figure 5.294 shows examples of chemo-crystallization. The increase in crystallinity can be linked to the formation of oxygen-containing compounds such as carbonyl, vinyl, and hydroxyl. These groups are formed in the amorphous zones and replace the carbon-hydrogen bonds [65]. Chemo-crystallization is terminated by branched and crosslinked structures and numerous structural irregularities in the amorphous phase, because these structures prevent the integration of additional crystalline structures [66].

After a particular loading time, the degree of crystallization is composed of the original degree of crystallization, crystalline growth due to physical aging processes, and recrystallization due to chain cleavage.

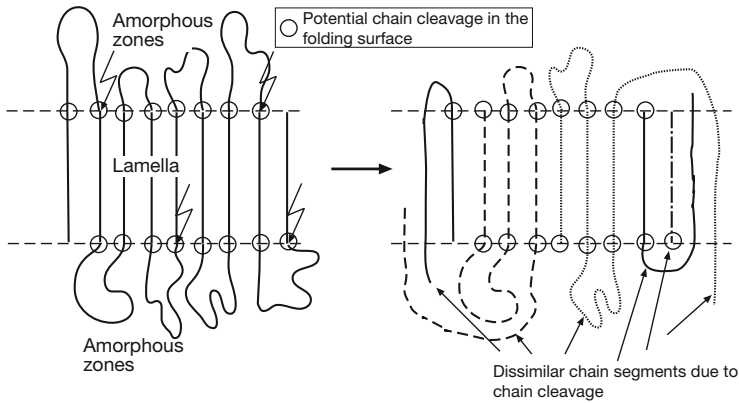


Figure 1.17 Chain cleavage and post-crystallization along the amorphous surface layer of lamellae [19]

1.4.2.3 Effects of Ozone

Despite its low concentration on the Earth's surface, ozone plays an important role in the aging of plastics and elastomers. Saturated hydrocarbons are largely resistant to ozone. Ozone plays a far more important role in the degradation of unsaturated plastics, where chain cleavage or crosslinking takes place, see Figure 1.18. Degradation caused by ozone (ozonolysis) can be compared to the effects of oxygen; however, it proceeds faster.

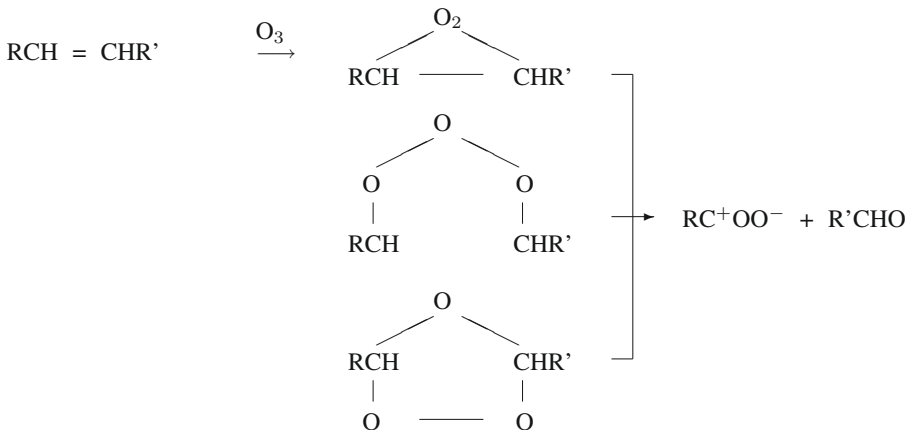


Figure 1.18 Influence of ozone: Creation and chemical effect of ozone on alkanes and alkenes [32]

The mechanism of ozonolysis can be described as follows: In the first step, ozone is added to the alkylene via 1,3 dipolar cyclo-addition. It forms the so-called primary ozonide (also called molozonide). Cleavage of the C-C-bond and of one of the two O-O bonds in the ozone (cycloreversion) leads to degradation of this ozonide into a carbonyl compound and a carbonyl oxide. They in turn form the so-called secondary ozonide by 1,3 dipolar cycloaddition.

A variety of products result from various reactions of the secondary ozonide: hydrolysis of the secondary ozonide forms primary carbonyl compounds. Because hydrogen peroxide is also formed during hydrolysis, it can further oxidize the products under certain circumstances.

The extent of the damaging effect of ozone strongly depends on simultaneously occurring mechanical loads. Without mechanical loading, a brittle surface layer is created in many plastics preventing further ozone penetration, whereas characteristic crack formation occurs in loaded elastomers; here, the growth mechanism resembles the craze formation in amorphous thermoplastics.

Ozone cracking depends on the degree of mechanical loading, temperature, and ozone concentration. At constant stress and temperature, the crack formation rate increases linearly with ozone concentration.

The temperature dependence of ozone cracking is a consequence of the influence of heat on a number of factors. With decreasing temperature, crack propagation generally slows down, especially in the temperature range of glass transition, because segment mobility is reduced or even frozen. Of particular interest is the fact that ozone cracking is accelerated by UV light, Table 1.11. Moreover, UV light activates not only the elastomer, but the ozone as well.

Conditions	Ozone (wt.%)	Time (min) to fracture at		
		15.6 N/mm ²	8.6 N/mm ²	5.7 N/mm ²
Ozone	0.4	19	33	100
Ozone + UV light	0.4	2	10	25
Ozone	0.8		40	
Ozone + UV light	0.8		22	

Table 1.11 Influence of the simultaneous effect of ozone and light on an elastomer under static load [67]

The mechanism behind the accelerating effect under mechanical load has not yet been entirely determined. The general opinion is that the continuity of the ozonized or oxidized surface layer is mechanically destroyed by warping and the newly formed surfaces enable further reactions between ozone and elastomer.

1.4.3 Influence of Water

The presence of water can influence both the polymer itself and any filler materials contained in it. This aspect has to be considered not only for parts in direct contact with water. Water plays a special role in the form of humidity or precipitation, especially in atmospheric aging, because water soluble degradation products capable of catalyzing further degradation are washed off. On the other hand, water also extracts water soluble additives. In addition, water can act as a plasticizer and be responsible for swelling and deterioration of plastics. The presence of water also tends to accelerate oxidation reactions.

1.4.3.1 Chemical Degradation (Hydrolysis)

The chemical effect of water (see Figure 1.38, Section 1.4.10.1) can be observed in particular in plastics with hydrolyzable groups in the backbone (e. g., ester, amide, and nitrile groups). The major hydrolyzable plastics of technical importance are polyesters (PET, PC), polyamides, and polyurethanes. Cleavage in the hydrolyzable groups leads to molecular weight reduction and thus to significant deterioration in their mechanical properties. Here, water alone does not have a severe deteriorating effect, but it accelerates hydrolysis in combination with catalytically effective acids or bases. The autocatalytic effect of acid groups formed by hydrolysis further accelerates it. Elevated temperatures also accelerate hydrolysis. To prevent hydrolysis during processing, these polymers have to be dried very well, and all traces of alkaline or acid reactants and metal ions have to be avoided.

Many polymers sensitive to hydrolysis are polycondensation products. During hydrolytic degradation, the polycondensation reaction is reversed.

Sorption and diffusion play an important role in the progress of deterioration. Therefore, physical structure is of great importance for this deterioration mechanism. It should be noted that hydrolysis in non-loaded parts proceeds relatively slowly. In loaded structures, e. g., in cracks, however, we observe clearly accelerated hydrolysis resulting in drastically reduced product service life.

Streaks and bubble formation in the molded part are typically the results of water vapor formation and water degassing during processing. Hydrolysis sensitive polymers are dried prior to processing. For some polymers, especially for polyamides, it has been questioned whether certain quantities of moisture under processing conditions have any hydrolytic effect at all, or whether disadvantages for the subsequent part result from the drying process, as it is an additional thermal load on the material. To date, there are no clear investigation results to show how the various drying methods affect polymer structure and thus their later service and aging properties.

1.4.3.2 Physical Aging Processes

The physical effect of water can be seen after water absorption by polymers: in the accompanying plasticizing effect and swelling, in changes in crystallinity, or in the extraction of additives.

1.4.3.3 Mechanical Effects of Water

Frequent changes in humidity can initiate mechanical effects caused by water. Cyclical shrinking and swelling can lead to crack formation. During a period of water absorption, the surface of the plastics part is wetter than its center. The surface tends to swell due to water absorption, but swelling is prevented by the dry core. Compression stresses arise at the surface while tensile stresses are present in the core. The conditions are reversed when a previously soaked part comes into a dry environment. Here, biaxial tensile stresses arise in the surface and corresponding compression stresses in the core [36].

The longer a plastic part is exposed to moisture, the deeper moisture will penetrate inside the material. The greater the difference between maximum and minimum humidity, the higher the stresses are. The penetration depth of these stresses depends on the frequency of moisture change. It can be calculated down to several tenths of a millimeter using the diffusion coefficients of most plastics that are on the order of 10^{-8} cm²/s [68].

In inhomogeneous plastics with components with differing capacities for water absorption, e. g., pigmented, impact modified, or coated plastics, mechanical stresses may occur, either temporary (various diffusion coefficients) or permanently (various saturation concentrations). These stresses act on the particular interfaces and can lead to delamination, cavitation, or also to the formation of haze due to differing refraction indices [36].

Mechanical stresses in interfaces strain the adhesion layers between materials that are often unstable, so that frequently observed signs of aging processes are peeling coatings and eroding pigments and modifiers [36].

Under weathering conditions, we often see deterioration profiles with circular external shapes, indicating the effect of drops of liquid. Here, hygroscopic liquids are often involved, such as alcohols or sulfuric acid (acid rain), which are better solvents than plastics, thus leading to the same moisture profiles and the same mechanical stresses caused by desiccation [36].

On the other hand, precipitation can also directly affect plastics mechanically, resulting in erosion or mechanical damage.

1.4.4 Influence of Mechanical Load

Mechanical degradation is defined as deformation caused by external mechanical loads resulting in changes in the bond angle and bond distance and thus in mechanical failure in the polymer chain [69].

How mechanical load influences the durability of plastics has not been entirely determined. On the one hand, high mechanical loads can result in chain cleavage and accelerate thermal-oxidative degradation, Table 1.12. On the other hand, mechanical loading can alter the physical structure in such a way as to retard diffusion processes.

Load (N/mm ²)	10 h			20 h		
	80 °C	100 °C	115 °C	80 °C	100 °C	115 °C
0	100	100	96	100	99	90
2	100	88	80	98	77	73
4	93	83	74	87	67	66
6	87	70	35	75	50	20

Table 1.12 *The influence of mechanical load on the change in strain at break relative to the initial value in polyamide 610 under thermal-oxidative exposure [70]*

Mechanical stresses in solid bodies can lead to chain cleavage and the formation of radicals. The alkyl radicals formed can create disproportionation, leading to unsaturated compounds or reactions with oxygen. For example, it was shown that mechanical load on polypropylene during extrusion at 230 °C created alkyl radicals [20], [69].

For polyethylene, polypropylene, and polytetrafluoroethylene it has been shown that mechanical stresses from grinding at -196 °C in absence of oxygen lead to the formation of micro-radicals due to bond cleavage between the C-atoms in the backbone.

Investigations into the UV resistance of polycarbonate films following radiation without mechanical load showed a drop to 40% of the initial data; the values dropped to 30% under mechanical load. Simultaneously, the changes in molar mass under tensile load are more significant than without load, Table 1.13.

Time (min)	M_w (g/mol) · 10 ⁻³	
	Unloaded	Loaded
0	26.9	26.9
15	24.7	25.0
60	24.7	23.7
120	24.4	21.9
240	21.0	18.9

Table 1.13 *Influence of radiation by a mercury vapor lamp on the molecular weight of polycarbonate in unloaded and loaded states [70]*

Other investigations on stretched polypropylene indicate that mechanical loads – both strain and stretch loads – during oven storage influence thermal-oxidative resistance positively compared to unloaded specimens, Figure 1.19 [71].

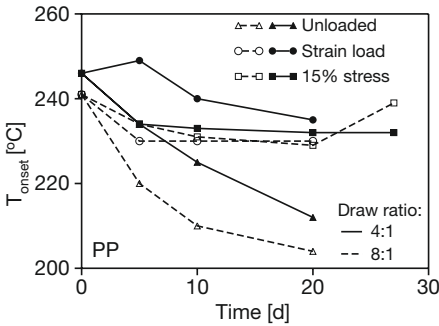


Figure 1.19
The influence of mechanical load during oven storage 130 °C on thermal-oxidative resistance in polypropylene (dynamic DSC-OIT) [71]

In addition to influences of mechanical load on degradation in polymer chains, unexpected degradation can occur due to the initiation of specific micromechanical processes and mechanisms. Such mechanisms (shear flow, craze formation, cavitation, etc.) are initiated in particular in inhomogeneous polymers (blends, filled and reinforced plastics, etc.) by inhomogeneous stress distributions caused by external mechanical loads. Typical examples for such physical aging processes are ABS materials with an unfavorable size distribution of rubber particles [72].

It is well known that ABS materials generally exhibit excellent toughness properties, permitting tough deformations and energy absorption even at very high mechanical loads. This behavior results from incorporated rubber particles that initiate many controlled microdeformation processes in the SAN matrix (craze formation and/or shear deformation, sometimes also formation of linear hole patterns) under load that lead to energy dissipation and characterize the toughness of ABS. However, entirely atypical brittle fracture has also been observed in ABS during mechanical tests following previous mechanical loading, i.e., following long-term mechanical loading clearly below ABS's actual failure limit (75% to 50% below failure limit). This phenomenon is observed in particular when there is a bimodal rubber-particle size distribution and the amount of larger particles in the ABS is small (large distances between rubber particles). Under long lasting mechanical load below the damage limit (during previous loading), isolated crazes are initiated, in particular by the large rubber particles. Thanks to their low propagation rate, these crazes may then circumvent existing crack stopping mechanisms. This creates craze structures (macro-crazes) that can grow to a critical size and thus lead to unexpected, premature, and brittle material failure, Figure 1.20 [72].

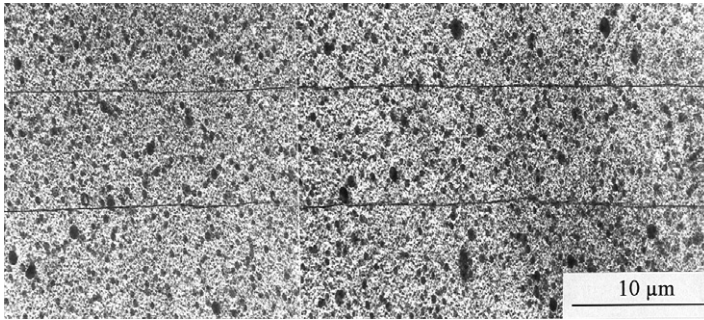


Figure 1.20 Crazes in an ABS specimen at 40% yield stress for 166 h [72]

Mechanical loads in the solid state are generally not critical at elevated temperatures (below glass transition or melting temperature), because plastics become increasingly ductile with increasing temperatures. One exception is the group of amorphous high-temperature resistant polymers. Polycarbonate, which is typically ductile, exhibits increasingly brittle failure under mechanical load at several 10 °C below its glass transition temperature. This effect results from internal damage caused by thermal disentanglements of the macromolecules. Thus, the micro-mechanical deformation mechanisms change from shear bands and/or homogeneous crazes to fibrillated crazes that are much more localized and smaller, thus leading to lower energy absorption (embrittlement) [73].

1.4.5 Influence of Chemical and Physical Structure

Although the influences of physical and chemical structure are presented separately in the following, they cannot be separated in practice. Changes in chemical structure will influence physical structure and vice versa.

The achievable results of investigating the influence of physical and chemical structure on plastics aging behavior are often limited by the production and preparation of specimens. In order to set, e.g., physical structures, processing temperatures must be varied which in turn affects chemical structure.

1.4.5.1 Influence of Chemical Structure

The chemical structure of a polymer is one of the factors that determine its reactivity, see Table 1.9. That is why polymers with saturated unbranched hydrocarbon chain structure are the most oxidation resistant, reacting extremely slowly with oxygen under normal conditions and in the absence of light. Even in the course of several years of exposure or service, these products do not change their properties. Although the bond energy of C-C-bonds is clearly weaker than that of C-H bonds, C-H bonds are attacked almost exclusively radically. Here, neither degree of poly-

merization, chain configuration, nor end groups is of real significance. However, oxygen sensitivity increases strongly in the presence of tertiary carbon atoms, such as in polypropylene. The oxygen sensitivity of a chain generally increases with branching; methyl or phenyl groups can then have a protective effect. The presence of neighboring C-H bonds activated by carbonyl groups also contributes to increasing susceptibility to oxidation, as in polyamides. Functional groups such as hydroxyl, ester, and amide groups can increase the susceptibility of plastics to chemical degradation. Thus, plastics with ester and amide groups are subject to hydrolysis, while plastics with hydroxyl groups are subject to dehydration. The least resistant plastics are those with double bonds, such as butadiene rubbers in ABS.

How polymers are manufactured influences their chemical structure, among other things. For example, there are various manufacturing routes for polyolefins that utilize different metal catalysts. The proportion of saturated and unsaturated bonds varies from one manufacturing process to another, depending on the number of end groups created. Chemical degradation, above all oxidation, is partly determined by the proportion of unsaturated bonds and metal catalysts (see Section 1.4.2.1.2) [56].

In addition, molecular weight distribution plays an important role in the thermal oxidation of plastics. For example, different polyethylene types with the same average molecular weight but different molecular weight distributions show that the rate of oxygen absorption is higher for the polyethylene with the broader molecular weight distribution. The number of methyl end groups is responsible for oxygen absorption. This correlates well with observations that branched structures (many end groups) oxidize faster than linear structures with the same degree of crystallization [56].

Chromophores such as contaminations, catalyst residue, and hydrogen peroxides formed during processing are some of the causes of UV light absorption, but they are also initiation sites for thermal oxidation.

Physical aging processes are influenced by chemical structure insofar as it is partly responsible for molecular chain length, tacticity, branching, and the arrangement of substituents. Thus, chemical structure influences the formation of physical structure and morphology of plastics.

Because the oxidation of plastics or the effects of chemicals involve a reaction between a solid or highly viscous and a gaseous (oxygen) or liquid phase, all reaction steps are diffusion controlled. Therefore oxidation and/or the effects of chemicals on plastics in the solid state are limited by the potential of the media to diffuse into the plastics.

The diffusion rate of media is considerably higher in amorphous plastics than in crystalline ones. It is influenced by segment mobility, i.e., by glass transition. In semi-crystalline plastics, the oxygen is not uniformly distributed, but is preferably

present in the amorphous regions. For PE-LD, for example, photo-oxidation proceeds much faster for materials with a low degree of crystallinity (35%) than in highly crystalline ones (42 and 45%). Diffusion is also inhibited when molecular chains can become oriented.

Media transport through plastics is based mainly on activated diffusion. It can also take place via submicroscopic capillaries present as micro-pores in the plastic. Activated diffusion is caused by thermal motion among macromolecular segments and associated with the presence of free volume. A diffusing molecule requires a certain amount of energy to travel from one point to another. This activation energy for transport is required to sufficiently separate the polymer chains connected with each other by Van-der-Waals forces so that the diffusing molecule can move; on the other hand, the energy is needed to form a new free volume. The possibility and ease of formation of free volumes is dependent on macromolecular motion. If chain motion is reduced, e. g., by the presence of groups that increase the cohesive energy between the chains, the permeability of the plastic material is decreased. A significant change in free volume occurs in polypropylene due to secondary relaxation (β -relaxation) at 80–100 °C, resulting in clear differences in degradation behavior above and below secondary relaxation [32].

Diffusion is a heat activated process that follows the Arrhenius equation (see Section 1.6.2.4):

$$D = D_0 \cdot e^{-\frac{E_D}{RT}} \quad (1.15)$$

- with D = diffusion coefficient
 D_0 = activation coefficient, corresponds to diffusion coefficients for $T \rightarrow \infty$
 E_D = activation energy of diffusion
 R = general gas constant
 T = temperature

In diffusion controlled processes, reaction rate increases with increasing permeability so that, in principle, the extent of degradation decreases as the degree of crystallization and molecule orientation increase.

1.4.5.2 Influence of Physical Structure

Physical structure is determined by material history and processing.

The existence of molecular free volume in amorphous plastics (and in part also in the amorphous zones of semi-crystalline polymers) has considerable influence on the engineering properties of these materials.

A glassy solidified plastic is not in a state of equilibrium, see Figure 1.8. This can be seen from the fact that, among other things, the material contains an excess amount of molecular free volumes during solidification. If this material is exposed to higher temperatures, yet still well below glass transition, the concentration of

free volume is quickly reduced and the state of the solid amorphous plastic approaches equilibrium. This also reduces the high molecular motion of the material, which is due to the free volume in the solid state, and it loses some of its potential for absorbing energy under mechanical load, i. e., it becomes more brittle. Annealing is a heat-treatment process to reduce residual stresses caused by temperature and/or crystallinity gradients after processing and helps the material reach thermodynamic equilibrium. Annealing leads to a reordering among the molecular chains together with a reduction in free volume. This is caused by releasing and rearranging physical bonds (such as hydrogen bridge bonds and van-der-Waals bonds) as well as by relaxing load bearing, entangled molecular chains [74]. Different manufacturing processes lead to different combinations of gradients in temperature and crystallinity, Table 1.14. Thermal gradients result when the temperature within a part is not uniformly distributed during processing and above all when external cooling is used immediately following the molding process. Gradients in the degree of crystallization result when the interior material experiences a different thermal history than the external layers [14].

Figure 1.21 shows just how strong this effect can be, using as an example a PVC-U annealed for different lengths of time (up to 100 h) at 65 °C. Strong reductions in yield strain can be seen, in particular after long testing times. But even at short test times, i. e., at high rates, the percentage reduction in ductility is similarly drastic.

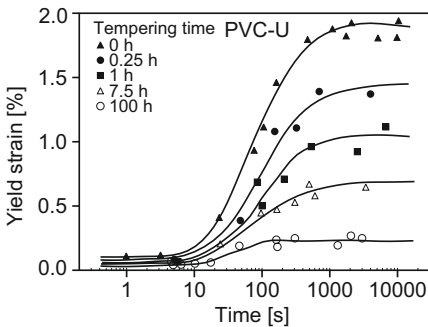


Figure 1.21
Reduction in yield strain in a PVC-U film after tempering at 65 °C [13]

Semi-crystalline plastics are usually annealed above their glass transition temperature and below their melting temperature, sometimes even quite close to their melting temperature range. Annealing leads to an increase in the degree of crystallization, a decrease in residual stresses, and a change in physical properties. The property changes are reflected in increased strength and Young's modulus, as well as in reduced ductility and stiffness. Extrudates or castings can be annealed in-line by controlled cooling or by a second reheating. Successful annealing usually requires reheating at a defined rate up to an appropriate annealing temperature and then holding this temperature until the thermal gradients and remaining stresses, as well as volumetric deformations have relaxed to an acceptable level (see Section 5.4.3.8) [14].

If embrittlement is not desired, a lower annealing temperature is often advantageous. Lower annealing temperatures result in reduced remaining stresses and thus to smaller changes in the degree of crystallization and less property changes. Higher annealing temperatures are often used to ensure higher dimensional stability at elevated temperatures. This leads to volumetric change together with crystalline growth. Tightly packed crystallites develop within a non-crystalline, low density phase. These differences in density can lead to volumetric deformations and local stresses, see Table 5.49 [14].

Degradation in plastics is characterized by a heterogeneous process. On the individual scale, chain cleavage takes place exclusively in amorphous zones, while molecule chains within crystallites are protected.

An increased degree of crystallization and/or orientation, however, also reduces radical mobility or disproportioning of the macro-radicals, increasing chain propagation and molecular cleavage. This effect works against oxygen mobility, and often makes it impossible to predict which effect will be dominant. That is why there is a discussion whether the influence of physical structure on chemical degradation depends on oxidation conditions. One of the problems involved in interpreting investigation results is that the production of highly crystalline specimens often requires the reduction of molecular orientation.

	Casting	Profile extrusion	Injection molding
Processing parameters			
Heat	Preheated, liquid phase	Screw plasticizing	Screw plasticizing
Pressure	Atmosphere	Medium	High
Viscosity	Low	Highly	High
Flow rate	Medium	Very slow	Fast
Shearing rate	Low	Low	High
Flow orientation	Very low	Low	High
Body temperature	Below T_m	Close to T_m	Above T_m
Time at T_k^*	Medium (min)	Long (min)	Short (s)
Cooling rate	Medium/slow	Slow	Very fast
Resulting gradients			
Degree of crystallization	Low	High	Mixed
Thermal, bulk	Low	High	Very high
Thermal, surface	Medium	Medium	Very high
Skin thickness	—	—	0.1 to 1 mm
Molded part			
Thickness	Thick	Thick	Thin
Remaining stresses	Medium/low	High	Mixed

Table 1.14 Processing parameters for various processing methods and their influence on stress distribution in manufactured parts; T_k^* : temperature of max. crystallization rate [14]

In oriented semi-crystalline plastics, embrittlement is anisotropic, Figure 1.22. In non-aged films, it is expected that their tensile strength in machine direction is lower than transverse to machine direction, because some reserves of plastic deformation are stored there. This situation can change due to degradation. After a certain exposure time, the values of strain at break in and transverse to the direction of orientation change their order. Strain at break is less susceptible to radiation in the direction of orientation than transverse to it. Various models describe this phenomenon, although none of the models has been generally accepted, because different mechanisms often occur simultaneously, and this has not been fully described [75].

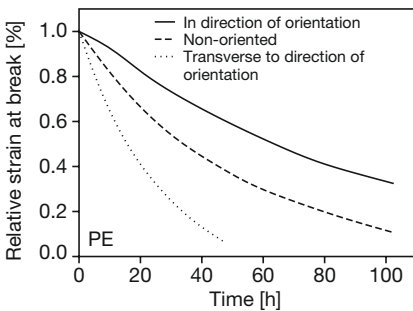


Figure 1.22
Anisotropy of photo-oxidative degradation in oriented polyethylene film [75]

The *Juska and Harrison* model explains the anisotropy of degradation on a molecular level and is based on the presence of amorphous structures under stated conditions. The load bearing, stretched molecules in this model are part of the crystalline zones and therefore not affected by degradation, at least during the first stage of degradation. They ensure mechanical continuity of the material in this direction, so that not only strength, but also strain at break is less influenced. Moreover, oxidation rate as a function of molecular stretching reaches a peak that coincides with the beginning of flow, Figure 1.23 [75].

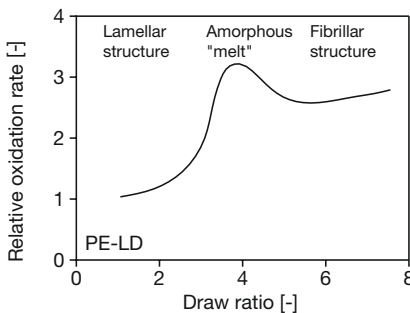


Figure 1.23
Influence of the stretching ratio on oxidation speed during photo-degradation of PE-LD [75]

The *CG model* (*Cook-Gordon model*) of crack blunting does provide a plausible explanation for macroscopically observed effects. In fact, in oriented polypropylene and polyethylene films a tendency to fibrillize following storage under UV

radiation has been observed. When cohesion in the transverse direction is reduced by degradation, the CG mechanism is reinforced and the strength and ductility of the materials is less influenced in the direction of orientation than transverse to it. However, if longitudinal strength decreases below a critical value, the CG crack blunting model is no longer effective, and dramatic embrittlement occurs in the direction of orientation. Such embrittlement is reinforced by external loading, Figure 1.24. In this case, a system of cracks develops at right angles to the direction of stress that strongly influences strength and stiffness [75].

Physical aging processes follow the same mechanisms explained in Section 1.3.4.

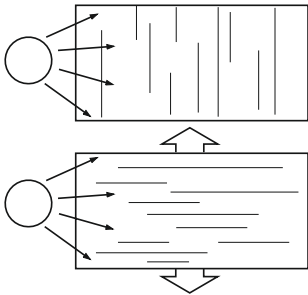


Figure 1.24

Model of photo-oxidative degradation in oriented semi-crystalline plastics; top without external load, degradation takes place between crystal fibrils; bottom a system of transverse cracks develops under external load [75]

1.4.6 Influence of Production Method, Catalyst Residue, and Metallic Contaminations

Metallic contaminations can accelerate chemical degradation (see Section 1.4.2.1.2). Metals introduced by contamination during reaction, in storage silos, or due to friction at the walls of the processing machine during processing can act catalytically. Metal ions then cause the degradation of hydrogen peroxides under formation of radicals. The damaging effect of metals can be minimized by complexing with suitable stabilizers (see Section 3.6.3).

Degradation of PE-HD is determined by the content of double bonds in the polymer, because the hydrogen atoms near a double bond oxidize more easily than the hydrogen atoms in the CH_2 groups of the alkyl chain. The number of double bonds depends on the polymerization process, Table 1.15.

PE-HD polymerization process	Double bonds/1000 C atoms		
	RHC=CHR	RHC=CH ₂	R ₁ R ₂ C=CH ₂
Mod. Ziegler	< 0.02	0.03	0.04
Standard Oil	0.95	0.03	0.04
Phillips	< 0.02	1.05	0.03

Table 1.15 Double bond content in PE-HD polymerized by various processes [18]

1.4.7 Additives

Additives can have a protective effect, but may also promote degradation processes, see Table 1.16 [76]. Their effect depends on the type of additives and their possible treatment [77]. Both synergetic and antagonistic effects can arise in combination with stabilizers, so that the entire system of plastic-additive-stabilizer has to be considered with respect to its influence on degradation processes [76].

1.4.7.1 Glass Fibers

Glass fibers as well as fiber-matrix adhesion determine the failure behavior of glass fiber-reinforced plastics [78]. When liquid media are excluded, fiber failure is often dominant. Compared to non-aged material, matrix embrittlement can be observed under strictly thermal-oxidative aging and aging by UV light. However, fiber-matrix adhesion continues to be good, so that the cause of failure is fiber fracture, and matrix degradation does not influence fiber-matrix adhesion. Mechanical strength is therefore not influenced, and in part even increased, see Figure 5.95 bottom left.

In the presence of media, however, glass fibers can become exposed and fiber-matrix adhesion weakened (Figure 1.25 right), which reduces mechanical properties. This behavior, also known as the “wicking”, is caused by the initial formation of microcracks in the plastic surface. The medium penetrates the material via such microcrack along the glass fibers, thus weakening fiber-matrix adhesion.

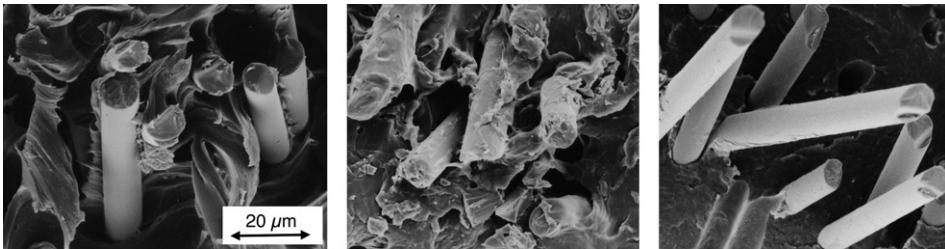


Figure 1.25 Influence of aging conditions on fiber-matrix adhesion in glass fiber-reinforced plastics; scanning electron microscopic images of fracture surfaces (tensile test)

Left: non-aged polyamide 66-GF30

Center: polyamide 66-GF30 aged in air (9 days, 160 °C)

Right: polyamide 66-GF30 aged in water (6 days, 140 °C)

Measurements of oxygen absorption in reinforced and unreinforced polyamide 46 indicate that oxidation is not influenced by glass fibers, Figure 5.215. Nonetheless, the expected service life of glass fiber-reinforced polyamide 46 is typically longer than that of the unreinforced material, Figure 5.214 and 5.215. Moreover, the influence of glass fibers on aging behavior was detected in specimens of different thickness. Doubling the wall thickness of an unreinforced polyamide 46 has no

influence on its service life, whereas the same increase in wall thickness doubles the service life of a 30 % glass fiber-reinforced polyamide 46. This effect is explained by the fact that in unreinforced materials, degradation at the surface is dominant, while it is subordinate in reinforced materials.

1.4.7.2 Fillers

Fillers such as talcum or calcium carbonate reduce the resistance of plastics to both air and chemicals if no suitable preventive measures are taken [79]. The main reason for the reduction in thermal-oxidative stability is partial sorption of the stabilizer system by filler particles, which reduces the availability of these substances in the polymer matrix.

However, fillers and additives may also delay degradation processes. The use of CaCO_3 in weathered filled and unfilled PE-HD illustrates how fillers can influence degradation reactions and thus delay the formation of carbonyl and hydrogen peroxide groups. They can also act as a protective layer against UV light [80], [81]. The effects of fillers and additives on degradation depend on the type of additives and on their pre-treatment [82].

1.4.7.3 Pigments

Pigments mainly affect weathering behavior because of their absorption behavior. All organic and inorganic pigments can therefore also provide protection against UV radiation. The extent to which this protective effect is dominant, or whether the degradation initiated by pigments is stronger, depends on numerous parameters, Table 1.16. A high degree of opacity of a plastic part ensures that damaging UV radiation cannot reach deeper lying layers of the material and cause changes in mechanical properties.

Crystal modification	Coating	Crystal size	Photo resistance	Time CI = 0.1 (h)	
				Oven aging	Radiation
PE-LD without TiO_2				3400	177
Anatas	None	Fine	Low	1800	46
Anatas	Low	Fine	Low	2570	100
Rutil	Low	Fine	Medium	1690	127
Rutil	Low	Fine	Medium	2260	156
Rutil	Low	Medium	Good	2750	233
Rutil	Medium	Fine	Very good	2957	156
Rutil	Medium	Medium	Very good	2120	175
Rutil	Strong	Medium	Excellent	2720	223
Rutil	None	Fine	Low	2957	82

Table 1.16 Influence of TiO_2 properties on oxidation in PE-LD at 60 °C (measured as the time at which a carbonyl index CI of 0.1 is reached) under oven aging and radiation [76]

The influence of pigments on UV stability of plastics is based on their absorption behavior in the UV light range and their interaction with stabilizers [83]. In pigmented systems, light resistance thus does not depend on the individual pigment, but always on the entire system. Light resistance depends on

- Pigment chemistry, Figure 1.26 top left and bottom right,
- Pigment concentration in the plastic, Figure 1.26 top right,
- Pigment distribution in the plastic, Figure 1.26 bottom left,
- Pigment physical condition, Figure 1.26 bottom right,
- Polymer grade and quality,
- Processing parameters,
- Layer thickness,
- Fillers and additives,
- Light stabilizers, Figure 1.26 bottom left,
- Intensity and duration of light exposure,
- Environmental influences (temperature, moisture, contaminations) [84].

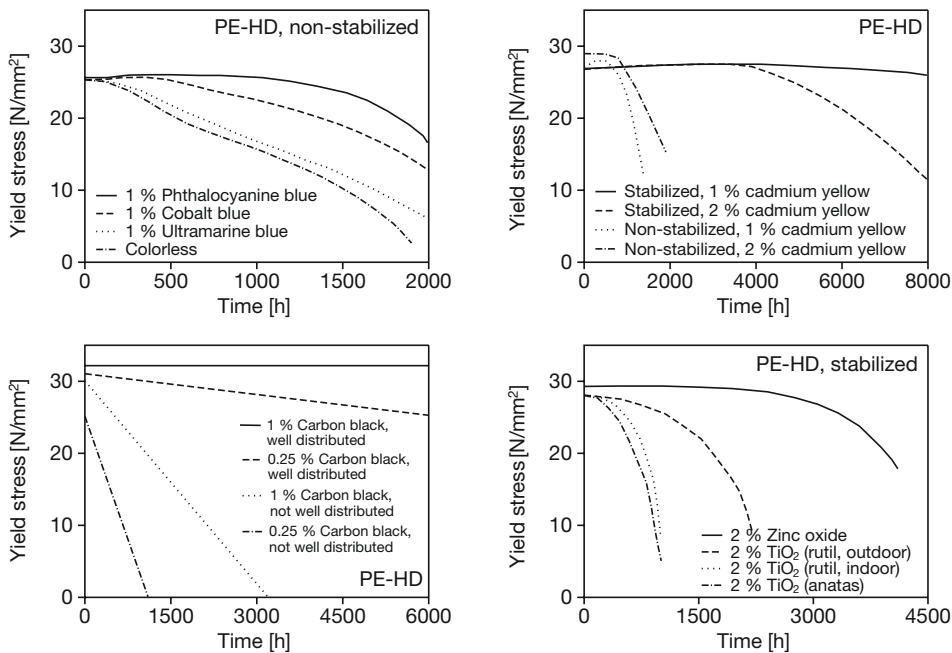


Figure 1.26 Influence of pigments on weathering resistance of PE-HD investigated in a weatherometer [83]

Top left: influence of various blue pigments

Top right: influence of pigment and stabilizer concentration

Bottom left: influence of pigment distribution

Bottom right: influence of various white pigments and their structure

Table 1.17 shows the influence of different color pigments on weather resistance of PE-HD [18].

Among common crystal modifications of titanium dioxide (anatase and rutile), only the rutile form is significant for pigmentation, because anatase exhibits considerably stronger oxidation capacity than rutile, Table 1.16 and Figure 1.26 bottom right. In addition, crystal size and surface treatment, as well as the photostability of the pigment used are of major influence.

Color	Type of pigment	Improvement
White	Stabilized titanium dioxide	30%
Yellow	Cadmium sulfide	30 to 40%
Orange	Cadmium sulfide/selenide	30 to 40%
Red	Cadmium sulfide/selenide	30 to 40%
Eurored	Cadmium sulfide/selenide	40 to 50%
Brown	Highly filled iron oxide	50 to 100%
Blue	Cobalt blue, ultramarine	30 to 40%
Green	Cobalt green	40%
	Chrome oxide green	40 to 70%
Black	Selected carbon blacks	> 500%
Natural	UV stabilizer	250%

Table 1.17
Improvement in weather resistance by color pigments compared to non-pigmented PE-HD [18]

However, not only light and weather resistance is influenced by pigments, but oxidation resistance as well, as shown by the example of a polyamide application. Pipes made from yellow polyamide 11 are used for gas lines. In these polyamides, phosphorous acid is often used as chain terminator. For reasons of environmental compatibility, the cadmium sulfide (CdS) used for many years has been replaced by a different yellow pigment, bismuth vanadate (BiVO_4). After a short time in service, pipes pigmented with bismuth vanadate exhibited obvious signs of oxidation. The reason for this premature aging was the formation of an oxidation-promoting catalytic substance from bismuth vanadate and phosphorous acid. Figure 1.27 (left) shows that the mechanical properties of the PA 11 are not influenced when cadmium sulfide is used as pigment, even at high concentration of phosphorous acid, whereas a clear reduction in mechanical properties occurs when the bismuth vanadate pigment is used. Figure 1.27 (right) shows that reducing the phosphorous acid content may delay aging, but the properties still change more significantly than when cadmium sulfide is used (at high phosphorous acid contents) [85]. Bismuth vanadate does not influence oxidation resistance in PA 12. This is probably due to differences in polymerization processes for PA 11 and PA 12, as well as to the use of different process regulators in the manufacture of PA 12.

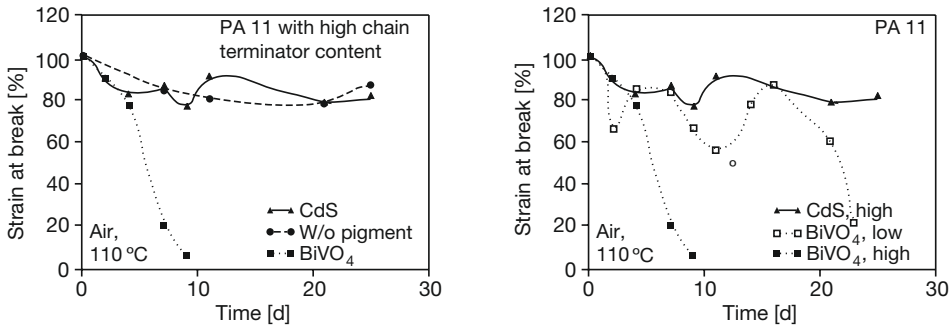


Figure 1.27 Influence of yellow pigments and phosphorous acid content on aging behavior of PA 11 [85]

1.4.7.4 Influence of Chemical Purity

High chemical purity is required of additives and fillers. They should contain no or only very few heavy metal ions, which can catalyze the aging process in plastics. Copper, manganese, and cobalt ions (see Section 1.4.2.1.2) influence thermal-oxidative and/or photo-oxidative stability of plastics negatively [86].

1.4.7.5 Flame Retardation Using Halogen Compounds

Currently, organic halogen compounds are still used in significant quantities to achieve flame retardation of thermoplastics.

The main disadvantage of many chlorinated compounds is their relatively high volatility and, in part, low thermal stability. Processing temperatures must be below 200 °C, although a slight increase is possible when adding PVC stabilizers. They bind chlorine ions freed during processing that can have a negative influence on the stability of flame retardant thermoplastics [86].

1.4.8 Effect of Radiation

1.4.8.1 Ultraviolet Radiation

Light waves acting on plastics can

- reflect on the surface,
- be dispersed in the mass and
- be transmitted and/or absorbed by the plastics.

Photochemical reactions result from the absorption of light energy by chemical structures. The radiation in sunlight that is effective on the Earth's surface and is the main cause of degradation in plastics lies in the ultraviolet range between 300 and 400 nm. The energy of ultraviolet light depends on its wavelength, Figure 1.28.

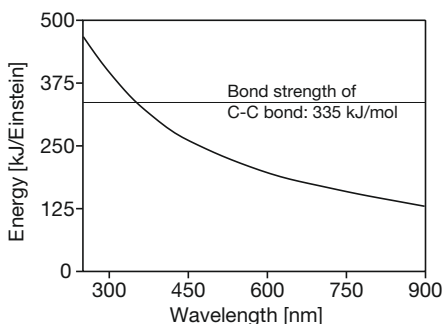


Figure 1.28
Energy (1 Einstein = 1 mol photon) of light radiation at various wavelengths [31]

At 350 nm, it is 343 kJ/mol. This amount of energy is sufficient to split many bonds (see Table 1.7).

The effects of UV light include chain cleavage, crosslinking, formation of monomers and other low-molecular compounds, as well as the alteration of existing functional groups, or formation of new ones.

Degradation in plastics due to UV light is mainly initiated by the effect of global radiation (direct and diffuse solar radiation). It is typically limited to a thin layer of material on the irradiated surface; only transparent samples show signs of degradation on the back side of the specimen. Global radiation covers the spectral range from $\lambda = 290$ to approx. $\lambda = 2,500$ nm. The photo-chemically very effective radiation with $\lambda < 400$ nm amounts to approx. 5 to 6%; more than 50% of UV radiation is diffuse radiation. Radiation intensity and spectral distribution depend very strongly on solar altitude, Figure 1.29. The radiation load on an existing material surface is also influenced by its specific geographic location and spatial orientation [87].

When a molecule absorbs UV light, it is highly activated for a short time. The excited molecule can transfer the absorbed energy to another molecule during collision or it can transmit the energy at a longer wavelength. Sometimes, the excited molecule initiates a photo-chemical reaction. Depending on its chemical composition, there is a wavelength range in which photo-chemical reactions are initiated for every material, Table 1.18.

Radiation energy has to be absorbed before it can initiate reactions. The frequency of absorbed radiation energy depends in part on the chemical structure of the irradiated material. Carbonyl groups in an aldehyde or in a ketone absorb at 187 and 280 – 320 nm, a C-C bond absorbs at 195 nm and in the 230 – 250 nm range; the hydroxyl group absorbs at 230 nm and primary C-C-bonds at 135 nm UV light.

Plastic	Effective wave-length of light [nm]
Polyester	315
Polystyrene	318 and 340
Polyethylene	300
Polypropylene, non-stab.	370 (280)
Polyvinyl chloride	310 and 370
Vinyl chloride-vinyl acetate copolymer	327 and 364
Polyvinyl acetate	< 280
Polycarbonate	280 to 305
Cellulose acetobutyrate	295 to 298
Cellulose nitrate	310
Polyamide	250 to 310

Table 1.18

The wavelengths of light that cause maximum degradation in various plastics [67]

Considering sunlight radiation impacting the Earth's, only carbonyl groups seem to act as UV light-absorbing groups. Non-degraded, pure polypropylene should thus not absorb any UV light and be photo-chemically resistant. However, if any double bonds or carbonyl groups are created by degradation processes during manufacturing, or if absorbent additives or catalysts are added, UV light absorbing conditions are present. The absorbed energy does not necessarily initiate a reaction at the point where it was absorbed, because it is transferred along the polymer chain and can attack at the weakest points. That is why, e. g., ether bridges can be cleaved although they do not absorb UV light [31].

The presence of a strongly absorbent group is not necessarily decisive for degradation. Acrylesters are resistant to UV light, but have a strongly absorbent carbonyl band.

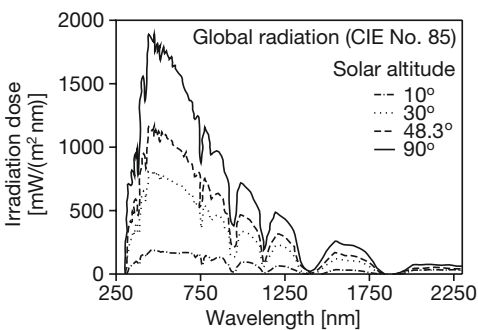


Figure 1.29

Spectral radiation intensity of global radiation depending on solar altitude [87]

Figure 1.37 shows a steep increase in molecular degradation in polyamide 6 for wavelengths below 300 nm. This does not mean that artificial weathering is accelerated by radiation with short-wavelength, energy-richer light. Radiation below the limit of natural global radiation at approx. 295 nm to 300 nm may provide misleading results, because unrealistic aging processes are initiated that are not found in practice.

Other climatic factors, such as heat, humidity, wetting and the composition of ambient atmosphere influence photo-chemical aging processes and the visible or measurable degradation result [87].

1.4.8.2 Ionizing Radiation

Ionizing radiation here means atomic or nuclear particles, such as γ -radiation, electrons, neutrons, and others. The intensity of such radiation on the Earth's surface is not high enough to influence plastics decisively, so that this radiation is only relevant in combination with a particular application, e.g., in nuclear plants, or when radiation is used for crosslinking or sterilization [88].

Ionizing radiation of plastics initiates primary processes, such as ionization of the polymer chains and chain cleavage, forming free radicals and in turn initiating secondary processes, such as decrease in molecular mass, weight loss, loss/reduction in crystallinity, or crosslinking. Cleavage and crosslinking can occur simultaneously, where one reaction dominates the other depending on the structure of the material and surrounding conditions. Chain cleavages dominate in, e.g., polycarbonate, polymethyl methacrylate, and polytetrafluoroethylene, whereas polystyrene, polyethylene, and polyvinyl chloride exhibit chain crosslinking [89].

In general, the lower the carbon contents in the polymer, the stronger its radiation sensitivity. Radiation sensitivity increases in the order: polystyrene, polyethylene, polycarbonate, polymethyl methacrylate, polyvinyl chloride, polytetrafluoroethylene [90].

1.4.9 Atmospheric Effects

The evaluation of atmospheric effects is problematic because of the large number of individual factors involved and the superposition and synergy between degradation products. Although light is often considered the main influencing factor, it is also possible that temperature is decisive [88].

The number of problems is almost inestimable, considering that different polymers react differently to different ambient conditions. This is illustrated by the fact that correlations between natural and artificial weathering found for one material do not have the same effect on other materials under the same conditions [88].

Moreover, the observed effects of weathering are dependent on the property under investigation. For example, strong discolorations may be accompanied by only slight changes in mechanical properties; or changes in microhardness (a surface effect) may be large compared to bulk changes, such as Young's modulus [88].

The aging behavior of plastics can only be roughly predicted by theoretical considerations alone. The quantitative influence of various climatic factors can only be determined experimentally. Chemical degradation due to weathering is influenced by the type and stabilization of the polymer, but also by many other parameters, such as the geographic location in use, orientation of exposure and the season of the year when climatic loading begins [87].

Photo-chemical degradation of plastics depends on the type of radiation or weathering as well as on additional parameters explained in detail in the following [87]:

- UV light (radiation strength and wave length)
- Temperature
- Moisture
- Neutral or acid wetting
- Mechanical loads
- Pollution, contamination
- Corrosive gases (NO_x , SO_2 , O_3)
- Prehistory.

1.4.9.1 UV Light

The statements made previously in Section 1.4.8.1 are valid here as well.

1.4.9.2 Temperature

Besides the general statements made in Section 1.4.1, the following aspects should be considered:

When evaluating the weather resistance of plastics, the surface temperature of exposed specimens should be considered. It is dependent on the intensity of radiation absorbed by the specimen, by ambient temperature, air-current conditions as well as by the distance of specimen from the substrate and by the nature of the substrate. Surface temperatures increase sharply as coloring varies from white to gray to black (see Table 2.10). Since oxidation is strongly temperature dependent, increased surface temperature will accelerate photooxidation progresses.

Surface temperature is essentially determined by the radiation balance at the specimen's surface, Figure 1.30.

On clear nights, effective exitance ($Q < 0$) can cause horizontal, thermally insulated surfaces to cool as much as $\Delta T = 15^\circ\text{C}$ below ambient air temperature. Black surfaces facing perpendicular to the sun's rays can heat up to as much as 80°C at $Q \gg 0$ (hot-house effects inside a passenger car can reach up to 130°C) [87].

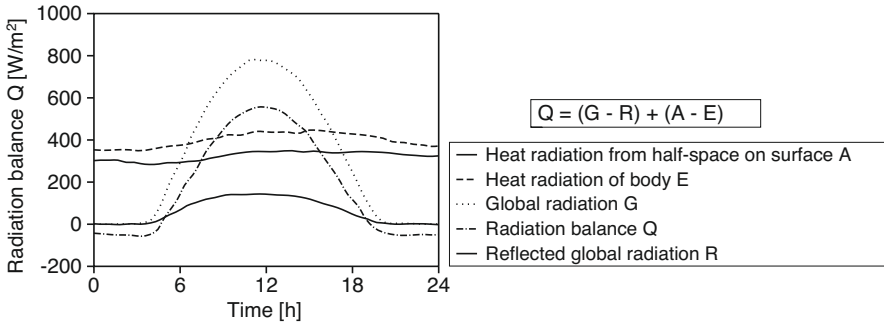


Figure 1.30 Daily progress of the radiation balance on a non-metallic, horizontally oriented surface with approx. 20% reflectivity (sunrise 4:00 am, sunset 8:00 pm) [87]

Figure 1.31, left, illustrates the temperature dependence of color change of a translucent PVC plate. While fading was measured on the sample surface at temperatures below 0°C , the radiance factor decreases as temperature increases above 0°C . Increasing yellowing and/or browning can be observed on the surfaces [87].

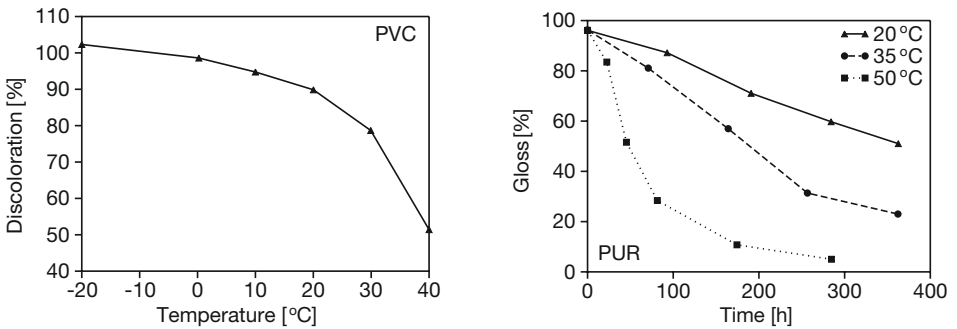


Figure 1.31 Influence of specimen temperature on
Left: PVC discoloration (determined using the radiance factor at 420 nm)
Right: gloss of a white PUR paint [87]

In this experiment, the specimen temperature was kept constant with considerable effort. In practice, even a slight discoloration leads to a further increase in surface temperature by radiation absorption and thus to a further increase in the rate of photo-chemical reactions, i.e., the influence of ambient temperature makes itself even more strongly felt in practice [87].

The temperature dependence of loss in paint gloss is shown in Figure 1.31, right. Here, white, oil-modified polyurethane paint was examined. Many aging phenomena exhibit comparably strong dependence on temperature. Temperature changes within the glass transition temperature range of a polymer may have very strong effects on aging test results [87].

1.4.9.3 Humidity, Water

Water vapor pressure or the dew point temperature in the lower atmosphere usually changes very little within 24 hours. Decisive for photo-degradation is, above all, the relative humidity in the interfacial climate at the irradiated surface. Because nights are cooler than days, relative humidity is higher at night than during daytime. Due to radiant warming on the surface by day, relative humidity often decreases to values below 10% relative humidity [87].

For nearly horizontal surfaces in particular, wetting time is determined less by rain than by nightly dew formation that can cause intensive wetting on about two out of three nights, even when it has not rained for days. Such surfaces are wet for approximately half of the year [87].

For non-transparent or non-translucent specimens, the relative humidity of the interfacial climate on an irradiated surface can be decisive for photo-chemical aging. Tests with PE-HD packaging showed clear influence of relative humidity on molecular weight reduction and carbonyl group formation, Figure 1.32 [87].

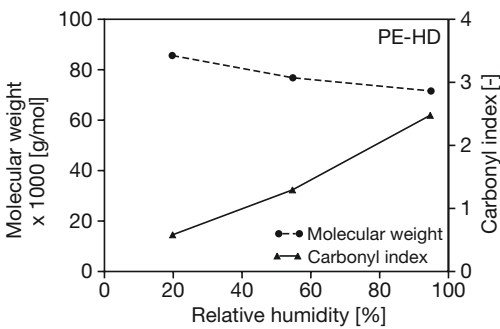


Figure 1.32
Influence of relative humidity on photo-chemical aging of polyethylene film after 72 hours irradiation time ($\sim 11 \text{ MJ/m}^2$ UV radiation) at 40°C [87]

The PVC shown in Figure 1.31 showed no influence of humidity. However, white PVC profiles showed strong influence of high humidity, caused by the photoactivity of TiO_2 [87].

Investigations into the influence of humidity on the light fastness of dyed and non-dyed fibers indicated that, given an increase in relative humidity from 45% to 85%, discoloration proceeds 250% faster in one material and 50% slower in another [87]. This shows that, for every combination of materials and climatic conditions, it must be determined whether humidity and water facilitate degradation or not. The duration of wetting and frequency of wet/dry cycles can influence aging test results to very different degrees [87].

The effects from dew and rain can also be reversed, as shown by the example of gloss decrease in a PUR paint, Figure 1.33. At 20°C , gloss decrease is higher from rain than from dew; at 50°C , the effect is reversed. The reversal of the effects caused by dew and rain occurs within the glass transition temperature range [87].

High humidity and accompanying droplet formation on the surface can cause a lensing effect that facilitates photooxidation.

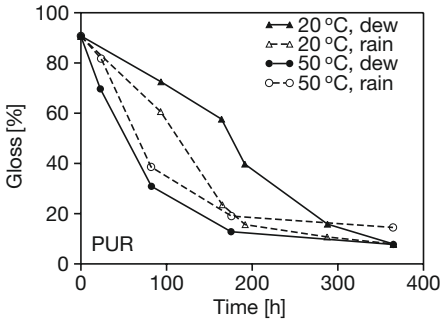


Figure 1.33
Influence of dew and rain on the gloss of a white PUR paint (determined by reflectometer readings) [87]

1.4.9.4 Corrosive Gases

Not only in strictly industrial areas, gaseous pollutants such as NO_x , SO_2 and O_3 are recorded in peak concentrations as high as 1 ppm [87].

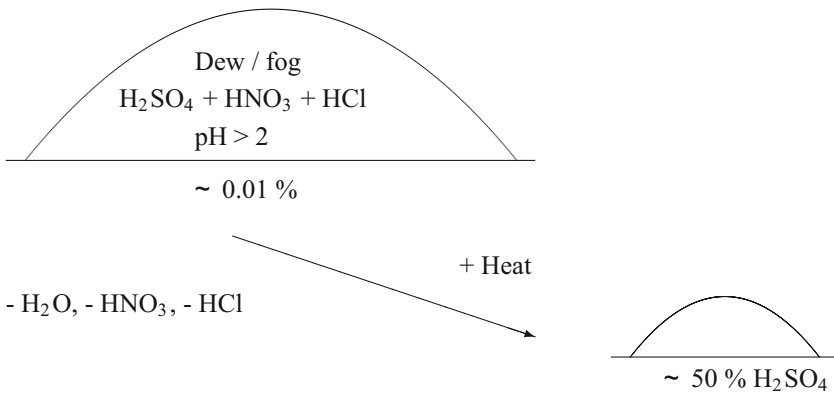


Figure 1.34 Formation of strongly acidic droplets on materials surfaces due to evaporation [87]

Air pollution can dissolve in atmospheric precipitation and deposit, e.g., as thin acid solutions, onto materials surfaces. Nitrous acid and nitric acid can form from nitrogen monoxide and dioxide in the presence of water and may lead to hydrolytic cleavage in plastics with ester and amid bonds. The products created from sulfur dioxide, sulfur trioxide and sulfuric acid cause hydrolytic cleavage in plastics with susceptible bonds, such as the amide bonds in polyamide.

In particular in fog and dew, peak values of $\text{pH} = 1.5$ are measured occasionally. Rain in Germany has an average pH -value of 4.2 and reaches a minimum value of 2.5. Due to the evaporation of highly volatile components, such precipitation can reach concentrations of $> 50\%$ sulfuric acid at increased temperatures (approx. 60°C), Figure 1.34 [87].

Figure 1.35 (laboratory experiment) and Table 1.19 show the influence of various gaseous air pollution on degradation behavior of various fibers used in textile weaves [91]. Tensile strength is already reduced even under UV light and exposure to clean air. The rate of property change depends not only on the type of material, but also on individual fiber thickness and weave structure [91].

Table 1.20 shows the influence of acid rain on various materials. Under strictly artificial weathering conditions, only polycarbonate and unstabilized polyamide 6 clearly exhibit graying. The other specimens show no visible changes. Acid rain (in the ADF test) leads to obvious changes in all materials. There are recognizable differences in the order resulting from acid concentration, especially between ABS and PBT specimens. ABS appears to react particularly sensitively to acid concentration, whereas PBT reacts to extended UV radiation.

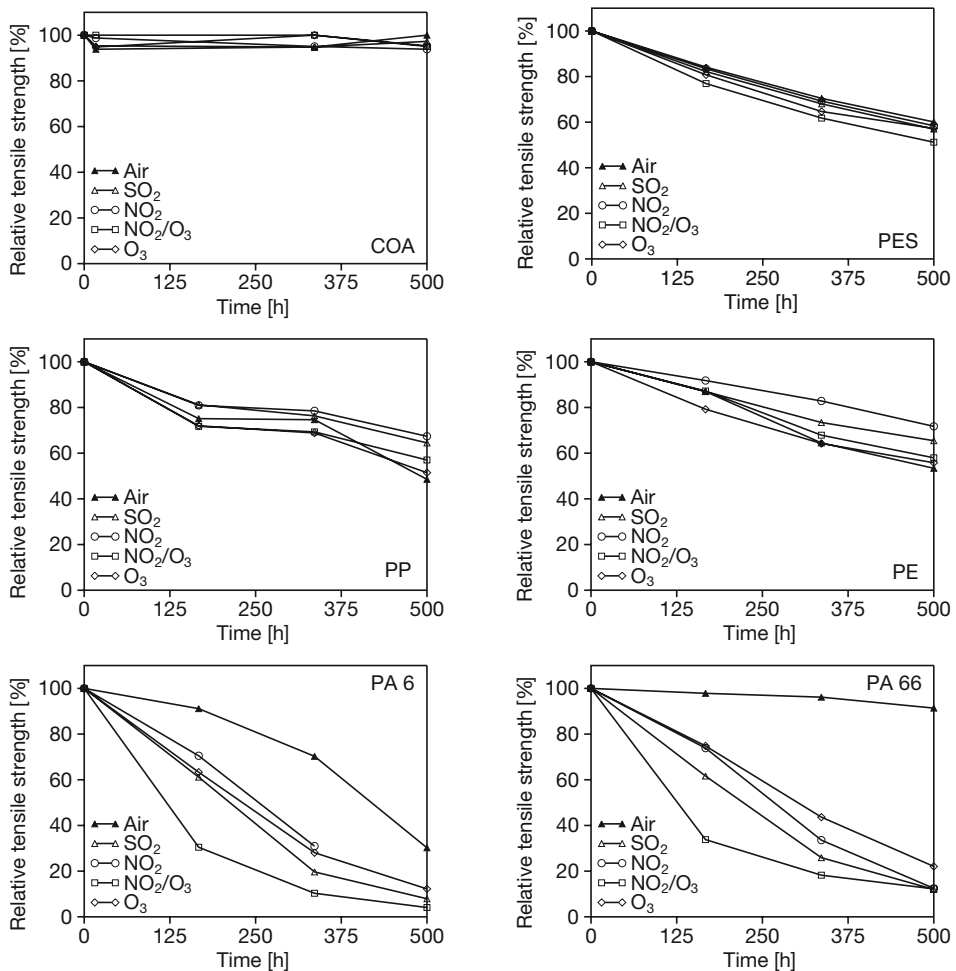


Figure 1.35 Reduction in tensile strength in various, undyed fibers in the presence of corrosive gases under UV light (290 - 450 nm); 50 °C, 70% rel. humidity (laboratory weathering) [91]

Location	Corrosive gasses ($\mu\text{g}/\text{m}^3$)				Temp. ($^{\circ}\text{C}$)	Radiation (W/m^2)	Time to 60% tensile strength (months)					
	SO_2	NO_2	NO	O_3			COA	PA 6	PA 66	PP	PE	PES
Härkingen	8.5	39.5	80.1	25.2	10.1	121.3	> 25	18	11	15	14.5	5
Lägeren	3.1	15.6	3.2	59.8	8.7	136.8	> 25	23	21	15.5	15	5.5
Dübendorf	6.4	31.0	21.8	36.0	10.2	118.6	> 25	16	13	13.5	13	5
Payerne	2.2	17.1	6.2	47.9	9.9	126.8	> 25	21	14.5	13.5	13.5	5
Bern	5.6	43.1	36.8	31.4	10.6	0	> 25	> 25	23	> 25	21	9.5
Sion	3.6	34.0	42.5	33.6	10.5	155.6	> 25	20	14	10	10	5
Cadenazzo	8.4	24.8	25.1	40.9	11.8	138.3	> 25	8	7	11	13	5
Davos	1.4	6.2	0.8	66.9	4.1	146.3	> 25	10	9	17	16	5

Table 1.19 Locations and their pollution and climatic conditions as well as their effects on various plastics; criterion: 60% reduction in tensile strength [91]

Material	Without acid precipitation ISO 4892 (1000 h)		With acid precipitation			
	Order	Median value for order no.	ADF (pH 1.7, 1000 h)		ADF (pH 2.5, 1680 h)	
			Order	Median value for order no.	Order	Average value for order no.
PA 6	3	3	9	8.6	9	9.0
PA 6, UV-stab.	1	1	6	6.0	5	4.8
PP	1	1	8	8.4	7	7.0
PC	2	2	5	5.7	8	7.9
PP-N, AO	1	1	1	1.6	1	1.8
ABS	1	1	7	6.2	2	1.9
PBT	1	1	3	2.6	6	6.1
PA12, type X	1	1	3	2.7	3	2.7
PA12, type L	1	1	4	3.2	4	3.8

Table 1.20 Comparative weathering of various plastics representative for external automotive applications according to ISO 4892 (1000 h) [198] and ADF tests (see Section 2.2.6); all samples were colored in high-gloss deep black and initially not visually distinguishable; average value of order number of the weathered samples (subjective sampling by 10 persons) [92]

The longer and weaker acidic test version enables better differentiation of the specimens. All specimens differ significantly from each other [92].

Microscopic images, Figure 1.36, of weathered samples illustrate the material-dependent influence of acid precipitation. The acidic weathered sample surfaces clearly exhibit the locally limited, additional effect caused by droplets of simulated acid dew. They include spots due to structural differences on PA 6, etching pits on PA12, or bizarre surface defects on the acid loaded ABS sample that indicate non-uniform material removal from the styrene and butadiene phases [92].

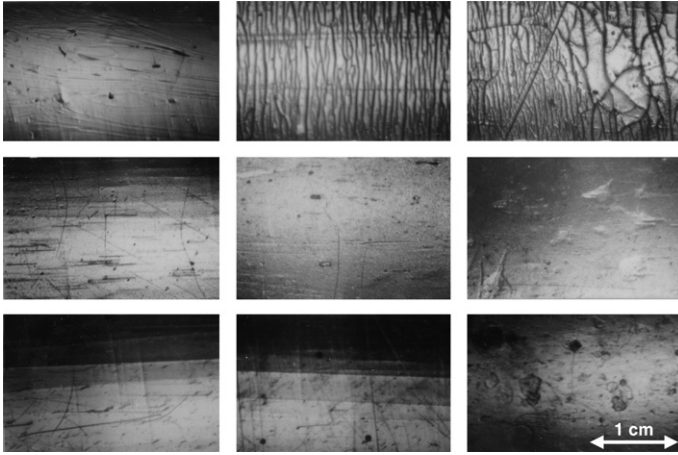


Figure 1.36 Microscopic images of the surface of polyamide 6 (top), ABS (middle), and polyamide 12 (bottom) following ADF test at various pH values [92]

Left: unweathered

Middle: 1000 h ADF test, pH = 7

Right: 1000 h ADF test, pH = 1.7

1.4.9.5 Solid Contaminations

Solid contaminations found in the atmosphere include dust, fine sand, carbon black and fly ash, whose effect on plastics predominantly is mechanical surface abrasion. Such surface roughing causes increased water absorption and deposits of contaminants, creating a suitable medium for microorganisms [32].

1.4.9.6 Material History

A material's history is often an important cause of differences in photo-chemical aging test results, Figure 1.37 [87]. Due to different histories, chemically identical plastic materials can exhibit different aging phenomena, even at exactly the same irradiation or weathering conditions.

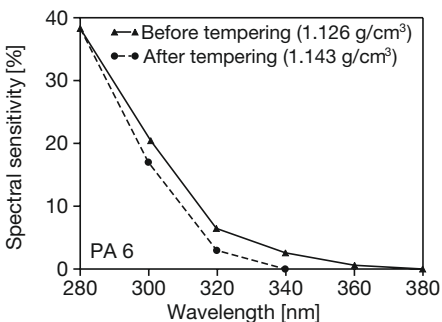


Figure 1.37

Spectral sensitivity of a PA 6 film prior and subsequent to tempering [87]

1.4.10 Influence of Chemicals

The resistance of plastic materials to exposure to chemicals depends on the chemical composition and structure of the plastic (composition of the polymer, composition and loading level of fillers and additives), on the composition of the acting medium, and on exposure conditions. Because reactions with plastics and elastomers take place in a heterogeneous system (solid/liquid or solid/gaseous), their progress is strongly influenced by diffusion processes [32].

The failure mechanisms of plastics under media influence can be classified into two groups analogous to the aging processes:

- Physical media influence (physical aging process),
- Chemical media influence (chemical aging process).

The two mechanisms differ in the way they influence plastics molecular structure. In the case of *chemical* media influence, once the material absorbs the medium, its molecule structure is attacked and altered, analogous to chemical aging processes. Typical examples of chemical media influence are hydrolysis and oxidation. Molecule chain shortening in hydrolysis, for example, results in embrittlement of the material [93].

By contrast, and analogous to physical aging processes, molecule structure is not attacked by *physical* media. Instead, interactions between the diffused-in medium and the molecular chains takes place. The increased toughness in polyamide due to water absorption is an example of physical media effects [93].

Here it should be emphasized that, in contrast to the effects of chemical media influence, *physical* media effects are reversible. However, component parts can also fail due to physical media effects, because incorporated media molecules may cause swelling of the plastics. Because media absorption is a non-stationary process, the outer area swells first, while the interior of the material remains unaffected. Internal stresses arise in the material which, beyond a certain strain level, can lead to cracking and thus ultimately to failure. However, desorption, not absorption, is the more critical factor here. Desorption may cause tensile stresses in the outer zones that result in cracking (see Section 1.4.3). Unless the microstructure of the material is damaged, swelling is a reversible physical media effect [93].

The various mechanisms rarely occur separately in practice. Instead, they overlap each other and often cannot be differentiated [93]. The damage caused by fluids may also accelerate oxidation in plastics [31].

1.4.10.1 Chemical Media Influence, Solvolysis

Characteristic of chemical degradation by chemical attack is the fact that even small chemical changes can initiate very marked property changes.

Solvolysis involves breaking a C-X bond in the backbone, Figure 1.38. Reaction partners for solvolysis include water, alcohol, ammonia, and others [20].

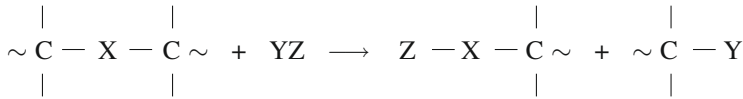


Figure 1.38 Backbone bond cleavage caused by solvolysis or hydrolysis ($YZ = HO-H$), with $X = O, N, P, S, Si$ [20]

Hydrolysis is a special case of solvolysis (see Section 1.4.3.1).

1.4.10.2 Physical Media Influence

The physical effects of fluids can lead to swelling, stress cracking, and/or extraction of additives in plastic materials.

1.4.10.2.1 Swelling

Figure 1.39, left, presents fluid absorption as a function of time. In diagram B, maximum equilibrium absorption is reached together with an increase in weight or volume. The dip in Curve A represents the extraction of soluble components prior to reaching equilibrium value. If extraction exceeds swelling, a decrease in volume or weight is observed, and equilibrium is reached with weight and/or volume below their initial values. Some materials show continuous volume and/or weight increase caused by oxidation (curve C).

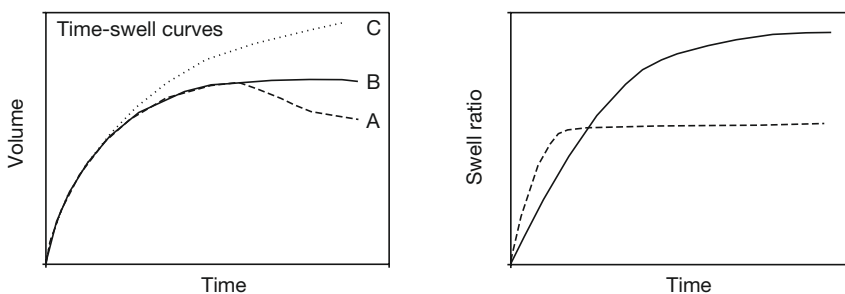


Figure 1.39 Swell behavior of plastics, swell ratio: see Eq. 2.12 [94]

Figure 1.39, right, shows that an absorption mechanism may result from either high maximum absorption at low absorption rate or low maximum absorption at a fast rate. This makes it clear that absorption generally has to be regarded as a function of time. However, if only a single value is obtained, it must be ensured that the

peak has already been reached. The time required for equilibrium depends on the particular plastic, the medium, and on test specimen thickness [88].

1.4.10.2.2 Stress Cracking

Fluids that have no significant effect on unloaded plastics can lead to crack formation when the plastic is under load. This phenomenon is known as stress cracking and is responsible for the failure of a large number of plastic components.

The various, standardized methods for investigating stress cracking can be classified in those with constant stress and those with constant strain (see Section 2.5).

1.4.11 Biological Influences

There are two types of attack by biological organisms on plastics: desirable and undesirable. Although some plastics (e. g., those with ester or amide structures) and/or additives have a chemical structure attractive to living organisms (hydrocarbons), undesirable attack is relatively rare. Nonetheless, serious problems may arise, mainly in tropical climates; therefore efforts are being made to create products for use in hot climates, e. g., elastomer pipe seals.

Biodegradable products are entering the market in ever greater numbers. They are designed to degrade by microorganisms relatively fast after use and do not pose ecological problems [88].

Among the most important biological influencing factors are microorganisms such as bacteria and fungi. These organisms are extremely versatile and adaptive; they produce an enormous variety of specific, degradation promoting enzymes. The rate of biological degradation depends on the ambient conditions: temperature, humidity, oxygen for aerobic bacteria and the absence of oxygen for anaerobic bacteria, as well as nutrients [95].

In addition to the functional groups, biological degradation depends on chain length and chain branching. Plastics that are originally not biologically degradable can turn degradable after chain cleavage caused by photo- or thermal-oxidative degradation [95].

■ 1.5 Influence of Processing and Application

Plastic component parts are manufactured or finished by various processing methods (e. g., compression, injection molding, extrusion, welding, etc.). During these processes, the molten plastic is exposed to thermal, mechanical, oxidative, and

hydrolytic loads of varying intensity at elevated temperatures. Such loads have decisive influence on internal material structure. In actual use, component parts, now in a solid state, are subject to further chemical and physical aging processes at much lower temperatures, often over long periods of time. Table 1.21 presents the various factors that influence aging during processing and in later use.

	Processing	Use
Temperature		
Polypropylene	250 °C – 270 °C	Short-term < 130 °C, long-term < 90 °C
Polyamide 6 and 66	240 °C – 320 °C	Short-term < 170 °C, long-term < 100 °C
Oxygen	Oxygen-poor	Oxygen saturation
Physical state	Liquid (melt)	Solid
Load times	Short-term	Long-term
R• concentration	[R•] >> [ROO•]	[R•] << [ROO•]
ROOH concentration	Low	High
Deterioration rate of ROOH	Fast	Moderate, temperature dependent

Table 1.21 Comparison of influencing factors under various aging conditions (processing, application) [38]

	Processing	Use
Radical formation due to:		
Thermal initiation	High	Negligible
Mechanical initiation	Dependent on conditions	Unexplained
Initiation by		
▪ Biradical ¹ oxygen	Little	None present
▪ UV light	Negligible	High under influence of light
¹ Biradicals: two unpaired electrons interact slightly or not at all		
Chemical aging processes		
Thermal degradation	Little	None present
Oxidative degradation	High	Dominant
Hydrolytic degradation	High in hydrolysis sensitive polymers	Dependent on hydrolysis sensitivity, temperature, milieu
Mechanical degradation	Unexplained	Unexplained, little, load dependent
Weathering	Irrelevant	Dependent on influence factors
Ionizing radiation	Irrelevant	Dependent on influence factors
Biological influences	Irrelevant	Dependent on influence factors
Physical aging processes		
	None present	Relevant, dependent on influencing factors

Table 1.22 Relevance of various aging processes during processing and in use

During the life span of plastic parts, oxygen-poor conditions dominate during processing, whereas oxygen saturation generally dominates during application [38].

Under oxygen-poor conditions, such as during processing, very few oxidized structures (carbonyl groups) are formed. This contrasts with aging under UV-radiation and/or in an aging oven where oxygen saturation is present during long-term loading [38].

In the following, polymer aging during processing is presented separately from aging during application. Although identical phenomena occur during both phases of product life, aging during use is decisively influenced by processing-induced morphology and pre-damage. Different phenomena dominate, however, due to variations in load intensity (Table 1.22).

1.5.1 Aging during Processing

Depending on the processing method used, plastics products made from one and the same material exhibit clear differences in their final properties. The production process determines, and/or influences the physical (degree of crystallization, orientation, and residual stress) and chemical structures (molecular structure and hydrogen peroxide concentration) in the component material. Because permanent use-properties result from the interaction between the structures present at the start of the product life cycle, service life is closely linked to the production process. Physical aging processes do not take place during processing. However, processing determines the physical structure of the finished part, thus influencing the physical aging processes and diffusion controlled degradation during use, Figure 4.1.

The oxygen diffusion, a determining factor in aging of solid bodies, can be neglected in screw-plasticizing processing methods, where air is mixed with the liquid melt [96]. Oxygen diffusion is significantly facilitated by processing methods with oxygen surplus, but without shear deformation, e. g., thermoforming.

Because polymers are oxidation sensitive, degradation typically takes the form of an oxidation process. However, its initiation can take place in different ways. The initiation reactions most important for processing include [97]:

- Thermally activated chain cleavage (see Section 1.4.1.2.1),
- Mechanically activated chain cleavage (see Section 1.4.1.2.3) and
- Attack by biradical oxygen (see Section 1.4.2)

The first two reactions listed lead to degradation, even without additional oxidation. The effects on long-term use properties are comparatively small, because higher molecular structures can be created by recombination reactions of radical byproducts. In addition, hydrolytic degradation can occur in hydrolysis sensitive

plastics (see Section 1.4.3.1). Oxidative degradation during processing leads to polymer chain cleavage and formation of macroradicals, Figure 1.13. The residual peroxides in the product influence its resistance during use.

1.5.2 Aging during Service

Under service conditions, primary radicals can usually be induced only by UV light. Primary radicals are not formed by temperature effects in the common applications range ($< 150\text{ }^{\circ}\text{C}$).

Primary radicals created by UV light react with oxygen as shown in Figure 1.13, where a variety of chromophores, mainly contaminations, increase UV absorption and thus facilitate aging.

Thermal-oxidative (and to some extent hydrolytic) degradation determines the degradation behavior of plastics in service. These are heterogeneous, diffusion-controlled reactions influenced by component thickness and physical structure of the material. Amorphous regions in plastics are not as dense as crystalline regions and determine the absorption and solubility of damaging media such as oxygen and water [98]. Thus, oxidation is heterogeneous in relation to substrate and peroxide concentration. Available oxygen content is decisive for the progress of auto-oxidation. If sufficient oxygen is present via diffusion processes, oxidation proceeds uniformly throughout specimen thickness. In semi-crystalline materials, the rate of both radical formation as well as oxygen diffusion depends on the degree of crystallization. If more oxygen is consumed locally than provided by diffusion, autoxidation slows down and can come to a halt [38], Figure 1.40.

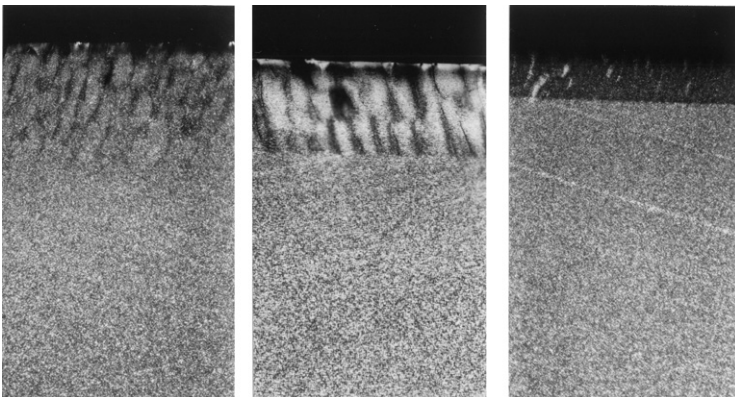


Figure 1.40 Influence of aging temperature on the oxidized surface layer in polyamide 66
Left: $140\text{ }^{\circ}\text{C}$; width of the oxidized surface layer $220\text{ }\mu\text{m}$
Middle: $160\text{ }^{\circ}\text{C}$; width of the oxidized surface layer $160\text{ }\mu\text{m}$
Right: $180\text{ }^{\circ}\text{C}$; width of the oxidized surface layer $95\text{ }\mu\text{m}$

Various authors have developed kinetic models based on Fick's Second Law in order to calculate oxidation profiles [38], Figure 1.41.

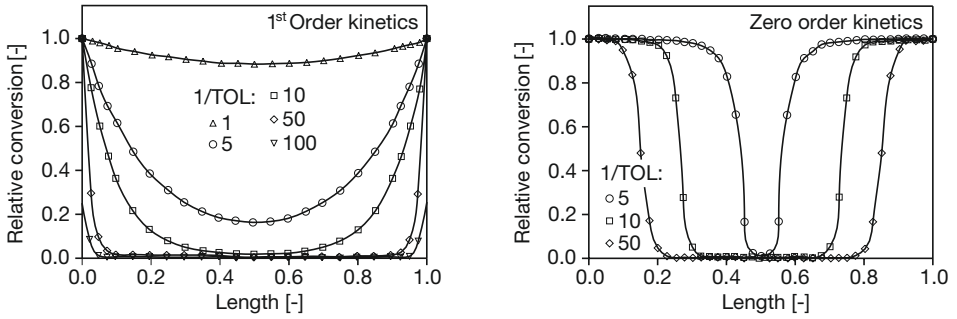


Figure 1.41 Calculated oxidation profiles for various kinetics; TOL: Total Oxidized Layer
Left: first order
Right: zero order [38]

In general it holds:

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} \quad (1.16)$$

with C = oxygen concentration
 x = perpendicular penetration at polymer surface
 t = time
 D = diffusion coefficient

If oxygen is depleted by oxidation, the concentration decreases.

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} - r \quad (1.17)$$

with r = oxygen reaction speed, $r = R(C)$

Local oxygen reaction rate is a function of local oxygen concentration. If degradation reaches a stationary state, then:

$$D \frac{d^2C}{dx^2} - r(C) = 0 \quad (1.18)$$

The oxidation profile can be derived from Eq. 1.18. The local change $P(x)$ in the test specimen layer and the change in cross section P are determined according to the following equation, where $r(C)$ is typically not known.

$$P(x) = \int_0^t r(C) dt; \quad P = \frac{1}{L} \int_0^L P(x) dx \quad (1.19)$$

Assuming first order kinetics, it follows that:

$$TOL = \left(\frac{D}{c} \right)^{0.5} \quad (1.20)$$

with TOL = totally oxidized layer (thickness)
 c = first order rate constant
 D = standard specimen thickness

Equation 1.20 agrees with Einstein's relation for the mean square of the path traveled by a molecule by diffusion in time t .

Assuming zero order kinetics, it follows that:

$$TOL = v \left(\frac{D}{c} \right)^{0.5} \quad (1.21)$$

with

$$v = \left[2 \left(1 - \frac{C_c}{C_s} \right) \right]^{0.5} \quad (1.22)$$

with C_c = critical oxygen concentration
 C_s = equilibrium oxygen concentration

The film thickness critical for uniform oxidation depends on the temperature and increases with decreasing temperature, Figure 1.42. While oxygen diffusion plays no role in films or fibers, it does play a role in thicker parts [38].

If aging is limited to the surface, microcracks may form. Crack propagation (under load) can continue into the interior of the material, Figure 1.42.

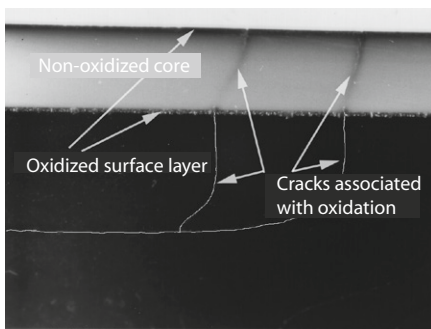


Figure 1.42
 Crack formation in oxidized polyamide 66
 (160 °C, 4 weeks)

As plastics age under thermal-oxidative load, there is a relationship between the increase in hydrogen peroxide concentration [ROOH] and the decrease in mechanical properties, Figure 1.43: At the start of thermal-oxidative degradation, hydrogen peroxide concentration is low. When hydrogen peroxide concentration increases

rapidly, a correlation between oxygen absorption and oxidation products (detectable by IR) is established; in polypropylene, a correlation between oxygen absorption and molecular weight reduction is detected. Table 1.23 shows molecular weight loss during the aging of unstabilized polypropylene [38].

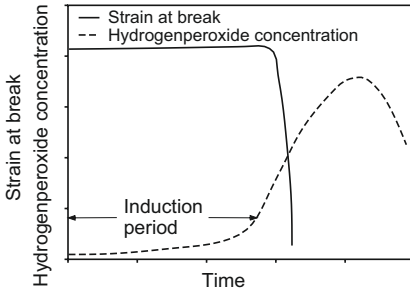


Figure 1.43
Connection between hydrogen peroxide concentration and loss of mechanical properties [38]

Time (h)	M_w	M_n	M_w/M_n
0	178,000	60,000	2.99
1	121,000	42,000	2.92
2	106,000	36,000	2.94
3	98,000	30,000	3.27

Table 1.23
Change in molecular weight and molecular weight distribution of unstabilized polypropylene after oven aging at 135 °C [38]

In summary, for aging during service:

- Primary radicals can usually be created by UV light only.
- Oxidation processes determine the service properties of plastics.
- The oxidation of plastics is heterogeneous.
- Oxidation profiles through the component thickness depend on oxygen diffusion and local oxygen consumption, both of which are dependent on temperature.
- The loss of mechanical properties is accompanied by molecular weight loss and surface cracking, as well as by crack propagation under mechanical load.

■ 1.6 Service Life Prediction

Even though service life prediction for plastics in terms of aging remains a much discussed and still unsolved issue, phenomenological approximations will be presented in the following, representing a step toward predicting service life. However, it must always be considered that it is scarcely possible to make precise predictions for the service life of plastics products, because the chemical reactions are complex and the physical and geometrical effects overlap (see Section 1.4.1).

1.6.1 Prerequisites for Service Life Predictions

In order to generate practical service life predictions – taking the mentioned limitations into consideration – two requirements have to be fulfilled: the conditions occurring in load tests and in service must be determined as exactly as possible; in addition, the criteria used for characterizing damage conditions have to be practical and meaningful, see Chapter 2.

1.6.1.1 Determining Influencing Factors

As a rule, it is impossible to simulate the aging influences occurring during service – except in practical tests. It is also problematic that the total effect of aging influences cannot be acquired by simply summing up the individual factors. In certain combinations, many influences counteract each other, but in other combinations, their effects may be compounding. Ignorance of the interactions between various influencing factors, or an excessive increase in the intensity of one factor can lead to an entirely different degradation mechanism and jeopardize the informational value of aging investigations and long-term predictions. Therefore, precise investigation into the interactions of occurring influences is required in order to improve service life predictions [99].

1.6.1.2 Characterizing Damage Condition

In order to predict service life, it is important to recognize and evaluate any induced material damage. A large number of analytical methods are available for this characterization, see Chapter 2.

1.6.1.3 Range of Extrapolation

Logarithmic axes and energy laws often make extrapolation look simple. Prior to every extrapolation, however, the model has to be validated and/or the range of extrapolation limited with the help of guidelines. Extrapolations should be performed only for a limited time or loading range. Considering temperature, for example, the degree of extrapolation depends on the precision of the model and on still acceptable uncertainties.

The generally accepted rule that extrapolations should not be performed over temperature ranges wider than 30–40 °C is based on these limitations. ISO 2578 [100] recommends limiting the temperature range to a maximum of 25 °C.

In general, extrapolations are not permitted over a physical transition range, such as the glass transition or the melting range. Similarly, extrapolations must not be performed if additional degradation mechanisms, e.g., due to excessive temperature increase, occur that the model does not account for.

1.6.2 Models for Service Life Prediction

An indirect way of predicting the duration of service is simply to compare materials under the available test conditions; the materials exhibiting fewer changes can be expected to last longer. If there is a standard material with known behavior in service, the behavior of other materials can be estimated. However, when time-compressing testing methods are used (see Section 2.1.1), this can be a dangerous assumption, because differences determined in this way do not necessarily reflect behavior in practice. In order to perform a direct determination of service life, it is necessary to apply an extrapolation method to the data measured [94].

When performing non-accelerated investigations, extrapolation is limited “only” to extended time, i. e., a time-dependent function is obtained for the change in one or more parameters [94].

When performing accelerated investigations, one or more aging promoting factor(s) is/are increased under service conditions. Here, it is decisive which factor(s) is/are selected and increased to which degree. Subsequently, any change in relevant properties is obtained as a function of time and dependent on other aging promoting factors, e. g., temperature. Aging can then be described by two approaches:

- By generating a function describing the rate of change of the relevant property over time,
- By generating a function describing the rate of change of the relevant property depending on concentration and level of the aging promoting factor.

Functions based on physical or chemical regularities are preferable to empirical methods. Such functions should not be more complicated than necessary to describe the observations [94].

Given these prerequisites, property changes can be predicted for longer times and/or lower concentrations of the aging promoting factors. The success of service life predictions depends on the quality and validity of the model used. Although a large number of models describing plastics aging have been available for a long time, they are rarely applied. Many accelerated aging investigations are performed on the basis of comparative investigations. One main reason for this practice is the fact that aging behavior depends on a large number of parameters, and the behavior of different plastics differs in its complexity [94].

1.6.2.1 Phenomenological Description of Aging

Damage (aging) is a cumulative process in plastics. Ultimate failure therefore results from an accumulation of material damage over the course of time. The defined shift factor (Eq. 1.10) generally depends not only on temperature T , but also on damage Q :

$$a = a(T, Q) \quad (1.23)$$

with a = shift factor
 T = temperature
 Q = damage

Thus, the time-temperature shift in Eqs. 1.7 to 1.11 is no longer valid. In many cases, the dependencies of temperature and damage can be separated, as suggested by Eq. 1.12.

Damage is determined by external conditions to which the material is exposed. In the simplest case, damage is a function of time, and temperature is as a parameter, see Figure 1.48:

$$Q = Q(t, T) \quad (1.24)$$

with t = time

We can now introduce a standardized damage Q^* with $0 \leq Q^* \leq 1$ in the following form:

$$Q^* = \frac{P_0 - P}{P_0 - P^*} \quad (1.25)$$

with P = property at time t
 with P_0 = property at time 0
 with P^* = property at the point of failure

The time dependence of standardized damage can then be represented in a scaled version, representing standardized damage as a function of a damage variable t/τ ($0 \leq t/\tau \leq 1$), where τ is the failure time of the material at temperature T or another external parameter:

$$Q^* = f(t/\tau) \quad (1.26)$$

with τ = failure time
 t/τ = damage variable

The variable t/τ depends on external conditions. The simplest function that fulfills $Q^* = 0$ for $t/\tau = 0$ and $Q^* = 1$ for $t/\tau = 1$, is an exponential function. In many cases Q^* can in fact be represented by such an exponential function:

$$Q^* = \left(\frac{t}{\tau} \right)^\alpha \quad (1.27)$$

with α = adjustment exponent (experimentally determined)

If the adjustment exponent α is constant, the time-temperature shift is very well approximated, see Figure 1.48.

In the most general case, however, the adjustment exponent α itself depends on the damage variable selected:

$$Q^* = \left(\frac{t}{\tau} \right)^{\alpha(t/\tau)} \quad (1.28)$$

This leads to a situation where, if adjustment factor α is a function of damage, the time-temperature shift is no longer fulfilled. In Eq. 1.28, the exponent changes continuously with damage. Equations 1.27 and 1.28 are shown in Figure 1.44. The solid line represents Eq. 1.28 with an adjustment exponent changing linearly with the damage. The dashed lines represent Eq. 1.27 with constant adjustment exponents for each line. The dotted curve represents a situation with long incubation time with a constant, but sufficiently large adjusting exponent.

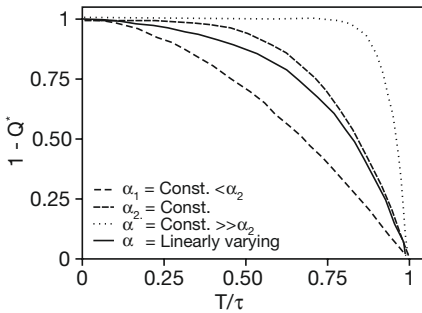


Figure 1.44
($1-Q^*$) as a function of damage variable t/τ

1.6.2.2 Standardized Processes

All standardized processes, such as IEC 60216 [101] and ISO 2578 [100] (see Chapter 2), consider temperature influence. In both cases, focus on finding the maximum service temperatures rather than extrapolating to normal ambient temperature. The new edition of ISO 11346 [102] for elastomers and thermoplastic elastomers also includes the Williams-Landel-Ferry equation model (Eq. 1.39) for time-temperature shift [94].

ISO 11403 [103] still has to be consulted for determining and expressing comparable multipoint data [94].

1.6.2.3 Models for Changes in Properties with Time

Time-dependent property changes in plastics can be exhibited in various ways, Figure 1.45, and depend on the concentration and degree of factors promoting aging as well as on the type of property selected. The simplest type of property change, a linear dependency, is unfortunately rarely found due to the large number of influencing factors. Any deviation from linear behavior can be caused by, e.g., addition of stabilizers, the occurrence of an induction period, or initial non-linear behavior caused by a tendency to seek a state of equilibrium. In addition, reactions can

superimpose: a chemical reaction can initiate linear change, while a physical effect can be logarithmic.

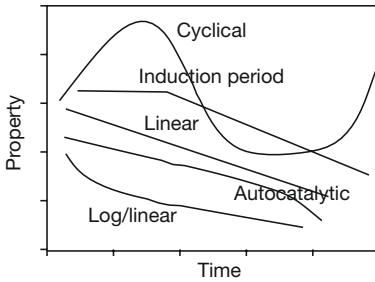


Figure 1.45
Property change in plastics with time [94]

An autocatalytic reaction exhibits an increasing rate of aging after a certain time period. Furthermore, cyclic property changes can occur, caused by the superposition of several reactions [94].

A general relation for property changes with time can be expressed as:

$$P = P_0 \left(1 - \frac{t}{t_0} \right)^c \quad (1.29)$$

with P = property at time t
 P_0 = property at time $t = 0$
 t = time
 t_0 = time at $P = 0$
 c = constant

This equation describes a change in property P which, starting from P_0 , deteriorates in the course of time to zero at time t_0 [94].

If the final value of P is not zero, the actual value can be entered on the right-hand side of the equation [94]. When

- $c = 1$: property change is constant,
- $c > 1$: property change for small t/t_0 is approx. equal to c and for $t/t_0 \rightarrow 0$ tends toward zero,
- $c < 1$: property change accelerates during aging.

In practice, this law cannot describe all aging reactions. However, it shows that aging does not necessarily have to progress continuously, but may take place discontinuously, e. g., after an induction period [94].

In some cases it is possible to transform the correlation into linear form by mathematical operations, such as taking the logarithm or taking a root. If the reactions are superimposed, it may make sense to consider only the main reactions and ignore other aspects, such as behavior prior to reaching a state of equilibrium [94].

It is general practice when comparing similar materials to ignore the shape of the curves and evaluate the times required for reaching a certain property limit value (e. g., 50% of the initial value). This may be useful, but it is less satisfying than creating a model and, when the curves are clearly different, can lead to false results [94].

1.6.2.4 Arrhenius Equation

Virtually all models currently used for describing the aging of plastics are based on the Arrhenius equation.

Exposure tests at increased temperatures based on the Arrhenius equation are state-of-the-art for evaluating the service life of plastic materials and plastics components. The Arrhenius equation has general validity and describes the temperature dependence of simple reactions and physical processes. The reaction rate constants of these simple chemical reactions increase exponentially with temperature. Thus, a temperature increase will cause an accelerated reaction.

However, if the Arrhenius equation is applied to complex reactions and processes with many individual reactions, it can lead to a distortion of the results, because the total activation energy of the combined reaction is influenced by the activation energies of the individual reactions so that the rate constant of the total reaction does not progress exponentially.

To apply the Arrhenius equation is to presume that the rate of plastics aging is determined by one (dominant) chemical reaction or one (dominant) physical process with corresponding dependency of aging rate on temperature. The relation found by Arrhenius for gas reactions between the reaction rate constant and absolute temperature T states that:

$$k(T) = A \cdot e^{-\frac{E}{RT}} \quad \text{or} \quad \ln k = -\frac{E}{RT} + C \quad (1.30)$$

with R = general gas constant
 E = activation energy
 k = reaction rate
 T = temperature
 A, C = constant

If aging rates measured at various temperatures are plotted logarithmically against $1/T$, the result according to this relation should be a straight line declining toward $1/T$. This is the Arrhenius presentation. If the data collected during accelerated measurements (at increased temperatures) are in a straight line, they can be extrapolated to normal service temperatures and thus to the aging rates occurring there (see Figure 2.21). Extrapolations can be performed with this method if there are sufficient data collected for the aging rate that exhibits sufficient linearity between their logarithm and $1/T$, and if the extrapolation range is not extended by

more than 40 °C with regard to ambient temperature or one decade with regard to service time. However, these extrapolations should be viewed critically, because they are easily misinterpreted when the activation energy is not temperature dependent over a wide range due to the overlapping of numerous competing reactions of various temperature dependencies (among them possibly rate-determining physical processes, such as oxygen diffusion).

The limitation of the Arrhenius equation is caused by the fact that it is applied to an unsuitable problem. The Arrhenius equation describes a simple chemical reaction, whereas the reactions are more complex in practice. In addition, it is presumed that the reactions at service temperature are the same as at test temperature, that activation energy is independent of temperature, and that chemical transformations relate directly to physically measured properties. If one of these assumptions is not valid, the Arrhenius equation is of limited use. Moreover, geometrical and physical effects are largely ignored.

If the curve progression of a time-dependent property is not linear, the following equation is usually applied:

$$f(P) = P^n \quad (1.31)$$

By combining this equation with the Arrhenius equation, we obtain:

$$P = P_0 \cdot \exp \left[-\frac{At^n}{n} e^{\left(\frac{-t}{\tau t}\right)} \right] \quad (1.32)$$

Equation 1.32 can also be expressed as follows:

$$P = P_0 \cdot \exp \left[-Kt^n \right] \quad (1.33)$$

or

$$P = P_0 \cdot \exp \left[-\left(\frac{t}{\tau}\right)^n \right] \quad (1.34)$$

with τ = failure time
 t/τ = damage variable

This is a so-called “stretched” exponential function with the parameters n and τ (or K). Parameter τ sets the time scale and n describes the “stretching” of the aging process over time. For $n < 1$, a wide transition results that narrows as n increases. Parameters $K^{1/n}$ or $1/\tau$ are rate constants that may exhibit Arrhenius-similar temperature dependencies.

Equations 1.33 and 1.34 are able to reflect the overlapping of several processes; however, they are valid only at the beginning of a damage process. As time progresses, exponential functions such as Eqs. 1.27 and 1.28 represent a decidedly better approximation.

Transposing extrapolations according to Arrhenius to applications in practice is also problematic because typically plastics are not exposed long-term to constant temperatures. Instead, they experience a complex time-temperature profile and plastic parts age more slowly at lower service temperatures than at elevated temperatures. The evaluation of these different loads can also be carried out according to the theory of aging progress using the Arrhenius equation. Here, service life periods at specific service temperatures (“aging shares”) are extrapolated to an increased test temperature using a scaling factor. Summation of aging shares results in a testing time that simulates the complex time-temperature profile. The simplest approach to solving this problem is to assume that the “damage” accumulates according to Miner’s Rule, Eq. 1.7. Prerequisite for this approach is that the same aging mechanisms act at all service and testing temperatures, i. e., that there is temperature-time equivalence. An essential problem in this approach is the fact that it is difficult to consider a memory effect – which in plastics is quite pronounced [104].

1.6.2.5 Time-Temperature Shift

As an alternative to the Arrhenius equation, property curves can be shifted along the time axis to create a master curve known from presentations of physical effects, such as creep at various temperatures. This approach is feasible when the property curves at different temperatures look similar. The shift of temperature dependent individual curves to a master curve is called *time-temperature shift* or *time-temperature superposition*.

The time compression corresponding to a time-temperature shift is then expressed using a time shift factor a_t . For any component property

$$a_t = \frac{t}{t_{ref}} \quad (1.35)$$

with a_t = time shift factor, reduction factor
 t = time after which a defined, identical property change has occurred
 t_{ref} = reference time after which a defined, identical property change has occurred

where t and t_{ref} are dependent on the particular load acting on the part [104].

By shifting the property curves that were determined at various temperatures along the time axis (usually log representation) until they are congruent, a master curve is obtained at an arbitrary reference temperature T_{ref} , Figure 1.46 [94]. The shifting results in a master curve for a time period considerably longer than that of the individual curves.

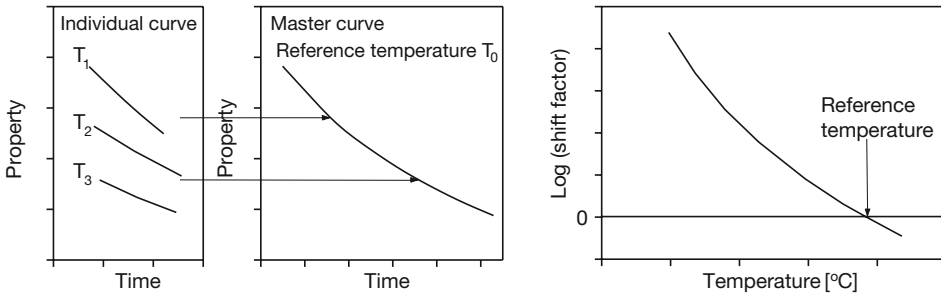


Figure 1.46 Time-temperature shift

Left: principle of a master curve

Right: temperature shift factor [94]

Mathematically, shifting the property curve means that the time at each temperature is multiplied by a temperature-dependent temperature shift factor a_T and that the property value is divided by the same factor.

The shift factor a_T can be acquired by

- the Arrhenius equation
- the WLF equation (Williams-Landel-Ferry equation).

The Arrhenius-equation describes the shift factors by a linear equation:

$$\log(a_T) = \left[-\frac{E_A}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (1.36)$$

To simplify the presentation in diagrams and enhance mathematical handling, the exponential function is converted to the common logarithm. Then:

$$a_T = 10^{k \left(\frac{1}{T} - \frac{1}{T_{ref}} \right)} \quad (1.37)$$

Where the activation factor k is defined as follows:

$$k = -\frac{E_A}{R} \log(e) \quad (1.38)$$

with a_T = temperature shift factor at temperature T
 k = activation factor
 E_A = activation energy
 R = general gas constant
 T = absolute temperature
 T_{ref} = absolute reference temperature

Here, the limitations of the time-temperature shift have to be considered when using the Arrhenius approach. These limits are mainly dictated by the following facts:

- Extrapolation must not straddle transition temperature,
- Attention to changes in activation energy due to changes in aging mechanisms,
- No extrapolation over too-large temperature changes (max. 15 Kelvin).

With the WLF equation the shift factors are acquired as follows:

$$\log(a_T) = \frac{a(T - T_{ref})}{b + (T - T_{ref})} \quad (1.39)$$

with T = absolute temperature
 T_{ref} = absolute reference temperature
 a, b = material-dependent constants
 (acquired with special curve fitting software)

1.6.2.5.1 Practical Application of the Time-Temperature Shift According to Arrhenius

The time-temperature shift principle using the Arrhenius approach (Eq. 1.36) means that a service time t at temperature T can be converted to a correspondingly shorter reference time t_{ref} at increased reference temperature T_{ref} , so that varying temperature profiles can be treated at constant load. This approach represents an engineering evaluation on a logarithmic time scale. Here it should be noted that absolute temperatures are to be used [104].

In practice, applying this time-temperature shift following the Arrhenius approach means that changes in characteristic material and component properties are measured at various temperatures over time. The recorded diagrams are called service life curves (property curves) in the following [104].

The display of these service life curves offers two different approaches:

- Exposing components at various temperatures and measuring the characteristic component part property at different test temperatures, Figure 1.47 left,
- Exposing component parts at various temperatures and measuring the characteristic component property at identical test temperature (typically room temperature), Figure 1.47 right.

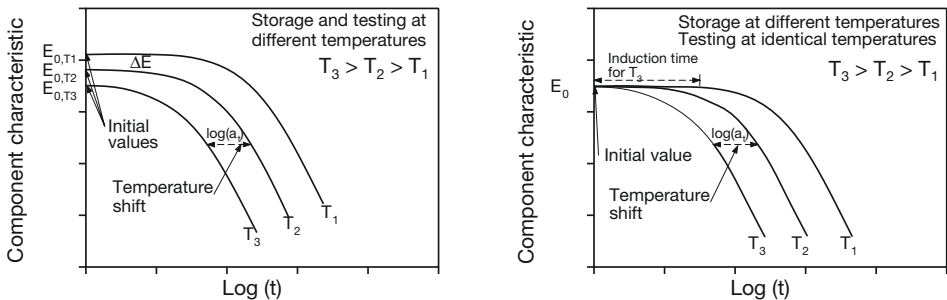


Figure 1.47 Service life curve with
 Left: different initial values
 Right: identical initial values [104]

With the first approach, the initial values at different temperatures will also be different, representing the initial value for the unaged sample. These initial values differ because the material properties change at elevated temperatures. Strictly speaking, these differences indicate the influence of physical aging processes [104]. Figure 1.47 reveals a superimposed shift on the property axis in addition to the shift on the time axis. If the change in property according to Eq. 1.40 is to be determined rather than the absolute property, the shift can be eliminated [104]:

$$\Delta P = P_{0,T} - P \quad (1.40)$$

with $P_{0,T}$ = initial value of the particular property P

In the second case, all curves originate from the same starting value, so that only the induction time (the time until the first reduction in the property measured) is shortened by elevated temperature, leading to an earlier recording of a decrease in property [104].

When displayed on the logarithmic time scale, the curves merge by shifting toward the x-axis. Here, the degree of shift represents the time compression, which can be described by the logarithm of the time shift factor $\log(a_t)$ according to Eq. 1.36. This means that the service life curves are equidistant when the difference between the reciprocal, absolute temperatures is equal [104].

It should be noted that strong variations in measured component characteristics are common. Therefore it is also feasible to apply various statistical methods, rather than evaluating the average values from several measurement. For example, it seems sensible to define a lower safety limit, ensuring that, e.g., 95% of the measured values exceed this limit [104].

The activation factors for defined levels of degradation are determined using the time-temperature shift. Here, the times at which a specific degradation level is reached are recorded for different temperatures. A logarithmic plot of these times against the reciprocal, absolute temperature provides the temperature-time curves. The slope of the temperature-time curve corresponds to the activation factor, Figure 1.48 [104].

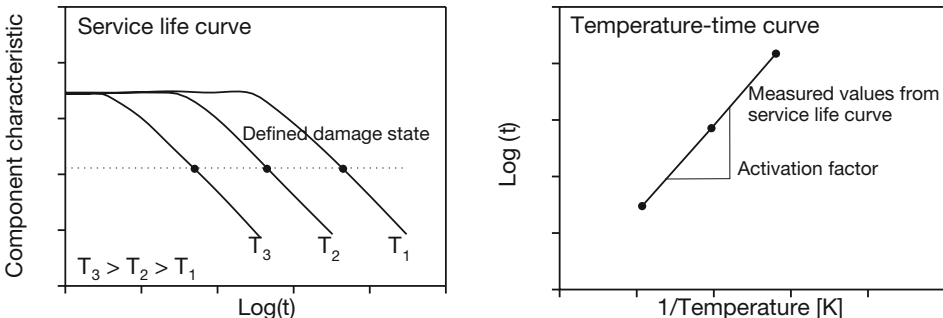


Figure 1.48 Determining the activation factor [104]

If the result of the temperature-time curve is a straight line, the activation factor is constant over temperature for the degradation level considered. If the temperature-time curve is not a straight line, the activation factor has changed. This indicates a change in activation energy and aging mechanism [104].

If the temperature-time curves are parallel for different aging states, the activation factor can be considered constant over time. Otherwise, a change in aging mechanism is involved [104].

The essential problem with the application of the principle of time-temperature shift using the Arrhenius approach is the fact that a change in activation energy cannot be considered together with changing aging mechanisms. This implies that Arrhenius extrapolations can be used only if the load is constant and there is no change in aging mechanism in the material. According to Figure 1.48, this corresponds to temperature-time curves represented by parallel straight lines [104].

This prerequisite, however, will apply only for the rarest of applications. The Arrhenius approach has to be carefully considered, in particular when loads are superimposed and temporally non-stationary [104].

1.6.2.5.2 Changing Temperature Load with Constant Aging Mechanisms

With an existing temperature-time profile, the time-temperature shift cannot be directly determined using the Arrhenius equation. In order to apply this approach, however, it is necessary to presume maximum service temperature for the entire service life. This approach would result in considerably over-dimensioned parts [104].

A better approach is to consider the individual time-temperature intervals of the given time-temperature profiles separately, and to use a weighted evaluation of these intervals regarding their contribution to the aging process in the component [104]. This procedure is analogous to the degradation accumulation hypothesis by Miner's rule, Eq. 1.7.

Every time-temperature interval is now associated with a degradation value according to Eq. 1.7. The sum of all degradation values corresponds to the total degradation of the material [104].

If the quotient of load time and failure time at the corresponding temperature is replaced by the reference time at elevated temperature, degradation accumulation can be formulated as:

$$t_{ref} = \sum_{i=1}^m t_{ref,i} \quad \text{with} \quad t_{ref,i} = t_i \cdot 10^{k \left(\frac{1}{T_{ref}} - \frac{1}{T_i} \right)} \quad (1.41)$$

with i = interval
 t_i = load time during interval i
 T_i = absolute temperature during interval i
 $t_{ref,i}$ = reference time

The sum of the reference times provides the total reference time for the time-temperature profile, Figure 1.49 [104].

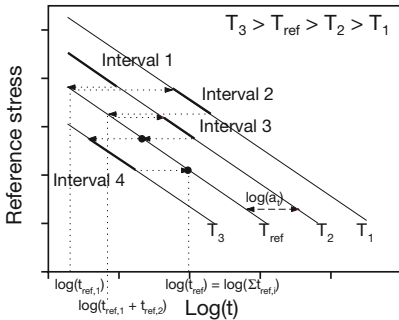


Figure 1.49
Theory of aging progress [104]

In this modified application of the damage accumulation hypothesis, degradation prior to reaching state “1” is not summed up to evaluate failure. Instead, the aging progress of individual intervals is related to the reference temperature and a reference time is calculated that corresponds to each of them. This reference time at reference temperature now results in degradation comparable to that in the time-temperature profile [104].

This principle is based on the following considerations:

- Exposure is defined as a temperature-time interval in which a constant load acts at constant temperature for a given time.
- Every exposure causes a change in the material that can be evaluated by the Arrhenius approach using the time-temperature shift principle.
- Such aging over an individual temperature-time interval in the time-temperature profile results in aging progress in the component.
- The sum of all individual aging progressions can be compared to the total component aging initiated by the given time-temperature profile.

1.6.2.5.3 Changes in Aging Mechanism

When the time-temperature shift is applied in the Arrhenius approach, changes or shifts in the aging mechanisms present the problem that extrapolations using a change in activation factor have to be performed, Figure 1.50 [104].

Figure 1.50, left, shows a schematic of a creep behavior diagram. Three different phases can be distinguished, each correlating to different aging mechanisms:

- Phase 1: Slight slope in the service life curve: Creep failure under high deformation caused by mechanical loading
- Phase 2: Steeper slope in the service life curve: Stress-crack formation with low deformation caused by physical interaction of water with the material
- Phase 3: Perpendicular drop of the service life curve: Oxidation caused by chemical interaction of atmospheric oxygen with the material

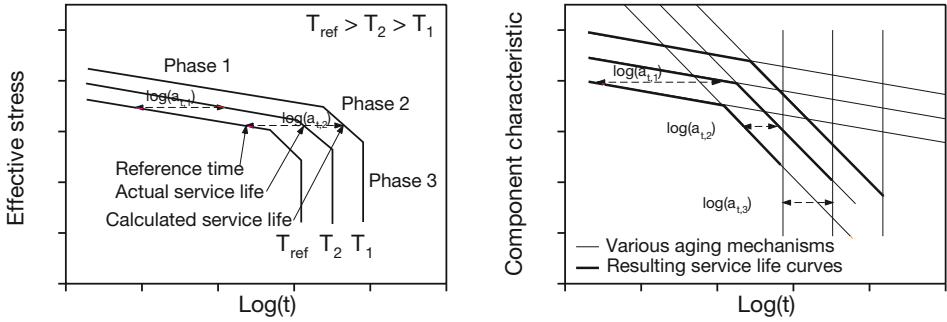


Figure 1.50 Changing aging mechanisms

Left: Schematic creep diagram

Right: Resulting service life curve [104]

Because every aging mechanism is associated with a specific activation energy, there are three different activation factors. For all aging mechanisms, the curves are parallel for different temperatures; only the distance between curves changes. The distance of the parallel shift is dependent on the activation factor and thus on activation energy [104].

While the activation factor represents a measure for the activation energy of the aging mechanism, the slope of the service life curve is a measure of the rate at which degradation progresses in the component. This rate may increase or decrease with a constant activation factor. In Fig. 1.50, this rate is constant for each aging mechanism, but increases with a change in activation factor [104].

According to Figure 1.50, right, the resulting service life always corresponds to the lowest value of the characteristic component value. The activation factor may increase or decrease with a change in aging mechanism. However, this is not valid for the slope of the service life curve, corresponding to the rate of degradation. The slope has to increase for all aging mechanisms, otherwise no change in aging mechanism would occur over time [104].

When all curves begin with identical initial values, the curves for the second aging mechanism also begin at this initial value. This implies that here the induction time is longer than it is for the first aging mechanism. After this induction time, these curves decrease with a stronger gradient. Here it should be noted that the initial value can never be precisely entered in the logarithmic presentation. Therefore, for short times all curves will asymptotically approach these initial values [104].

Consequently, the slope of the curves can be subject to change over time despite of a constant activation factor [104].

According to Figure 1.50, left, switchover points can be defined for the resulting service life curves at the individual temperatures. The aging mechanism and its

accompanying activation factor change at these switchover points. It is obvious that degradation increases with increasing activation factor at the switchover point for lower temperatures, Figure 1.51, left. Increasing degradation in this case is correlated with a decrease in measured component characteristics. Consequently, all switchover points are in a straight line [104].

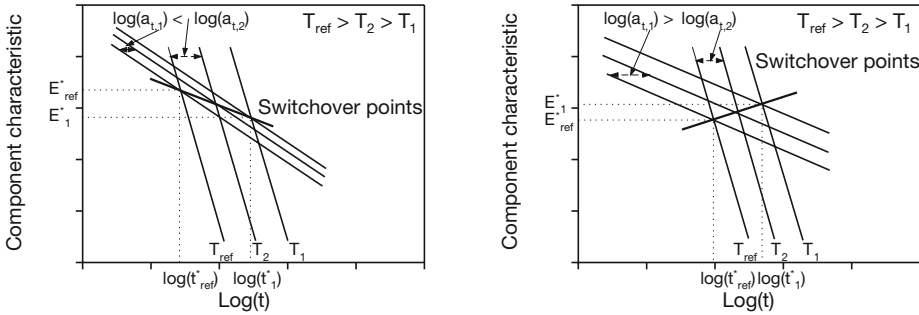


Figure 1.51 Switchover points for
Left: increasing activation factor
Right: decreasing activation factor [104]

Conversely, degradation decreases with decreasing activation factors, Figure 1.51, right. This corresponds to a higher characteristic value and results in an ascending straight line for all switchover points [104].

If the assumption is valid that the service life curves are straight lines, the time shift of the switchover point is:

$$t^* = \frac{t_{ref}^*}{m_1 - m_2} \left(m_1 \cdot 10^{k_1 \left(\frac{1}{T} - \frac{1}{T_{ref}} \right)} - m_2 \cdot 10^{k_2 \left(\frac{1}{T} - \frac{1}{T_{ref}} \right)} \right) \quad (1.42)$$

The characteristic component value at the switchover point at this temperature is:

$$E^* = E_{ref}^* + m_1 (t^* - t_{ref}^*) \cdot 10^{k_1 \left(\frac{1}{T} - \frac{1}{T_{ref}} \right)} \quad (1.43)$$

with * = notation for switchover points
 m = Slope of service life curves
 k = activation factors
 1, 2 = indices for particular aging mechanism

The slope of the service life curves influences the magnitude of the shift in switchover point. With increasing the slope of the curves, the shift in switchover point is less pronounced than when the slope increases more slowly [104].

These relationships, however, are valid only for temperatures below reference temperature. Above reference temperature, the influences are reversed [104].

In practice, service life curves corresponding to two to four temperatures are determined. They provide the activation factors and slopes for the different aging mechanisms, as well as the respective switchover points. They can be used to calculate service life curves at operating temperatures, Figure 1.52. These curves provide the basis for correctly determining reference time and activation factor [104].

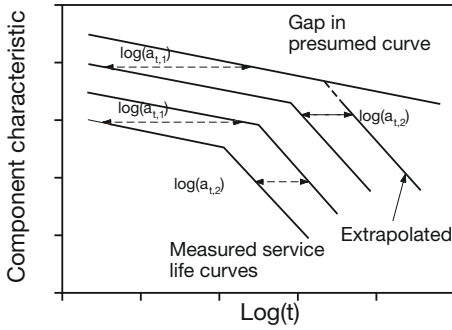


Figure 1.52
Extrapolated service life curve with gap [104]

It can be clearly seen that a gap in the service life curve is created when extrapolating to low temperatures. This can be explained by the fact that the progression of the service life curve for the second aging mechanism is not known prior to a certain degradation level. This level of degradation is lower than the switchover degradation at this temperature. Therefore it is not known how the extrapolated service life curve progresses in the transition range between both aging mechanisms [104].

In most cases, however, it can be assumed that the existing slope in the curve of the second aging mechanism can be extended. This is, however, only an estimation and has to be considered when the results are evaluated. When a curve has already turned into a straight line, extending this straight line is valid [104].

1.6.3 Dimensioning to Meet a Specific Service Life

1.6.3.1 Reduction Factors

Plastics in load-bearing parts are subject to various influences, sometimes changing their properties. The effects of load time and load type also have to be considered. Because the effects of the various loads are rarely measured comprehensively at their various levels and times, not to mention combinations, individual reduction factors are used to evaluate the overall effect [15].

1.6.3.1.1 Stress-Related Dimensioning

The basic equation for conventional dimensioning states that:

$$\sigma_{adm} = \frac{K}{S \cdot R} \geq \sigma_{max} \text{ or } \sigma_{fmax} \quad (1.44)$$

- with σ_{max} = maximum stress occurring under monoaxial load,
 σ_{fmax} = maximum comparative stress under multiaxial load calculated on the basis of a suitable failure hypothesis
 K = short-term strength value to be considered for dimensioning,
 S = safety factor,
 R = material reduction factor determining by how much the particular mechanical strength value has to be reduced in order to allow for specific, predictable loading conditions and influences from temperature, long-term load, dynamic load, processing, chemical attack, aging and others. It should also give the designer cause to consider possible strength-reducing influences. To this end, the factor R is divided into individual factors.

For example, the specification of admissible stress for a swimming pool pump takes the following form:

$$\sigma_{adm} = \frac{K}{S \cdot R_T \cdot R_{cr} \cdot R_{dyn} \cdot R_A \cdot R_W \cdot R_{no} \cdot R_{ws} \cdot R_{pr} \cdot R_{ex}} \quad (1.45)$$

- with R_T = loss of strength caused by temperature influence at 20 °C,
 R_{cr} = loss of strength caused by creep load (reference values: a few hours = 1.4; weeks = 1.7; months = 1.8; years = 2),
 R_{dyn} = loss of strength caused by dynamic load (1.3 to 1.7),
 R_A = aging influence (dependent on aging conditions and duration),
 R_W = water influence, e. g., for PA accompanied by considerable property changes,
 R_{no} = notching influence, higher under dynamic load than under static load, see Table 1.24.
 R_{ws} = weld seam, see Table 1.24 and 1.25.
 R_{pr} = influence from processing, under normal conditions 1.05 to 1.25.
 R_{ex} = uncertainty of determined data, e. g., when extrapolating, or inaccurate information on load (reference value: 1.1 to 1.3).

The number of reduction factors can be expanded according to load analysis. Table 1.25 shows the influence of injection molding orientation on drill holes and weld lines made from ABS [105].

The R factors listed in Table 1.25 are suitable for a general evaluation of reduction factors for semi-crystalline, amorphous, and glass fiber-reinforced thermoplastics.

If dimensioning is performed consistently and systematically, only the characteristic data acquired during short-term tests are suitable as characteristic measurement data (K values). They include yield point σ_y , ultimate strength σ_F for brittle material behavior, and the threshold for a particular non-elastic deformation $\sigma_{0.5}$.

Material	R_{dyn}	$R_{stat/Bo}$	$R_{dyn/dh}$	$R_{stat/BN}$	$R_{dyn/ws}$
ABS	-2.6; \perp -4.31 ¹⁾	—	4.4	—	3.4
PC	2.8	1.0	8.3	1.05	6.7
PC-GF30	2.6	1.1	5.5	1.0	4.0
PA 6 dry	1.8	1.0	3.0	1.0	1.8
PA 6-GF30 dry	2.5	1.4	5.4	1.75	4.5
PBT	1.7	1.0	2.0	1.0	1.8
PBT-GF30	2.1	1.3	4.6	1.3	4.0
Test specimen		Drill hole (dh)		Weld seam (ws)	

¹⁾ for tensile or tensile-swelling load in relation to injection orientation

Table 1.24 Reduction for static and dynamic load with additional notch and weld seam [105]

Thermoplastics	Static			Dynamic	
	Short-term		Long-term	$n \leq 10^7$	
	Once	Several times		Semicrystalline	Amorphous
Semi-crystalline (ductile)	1 \div 1.25 (1 \div 0.8)	1.25 \div 1.7 (0.8 \div 0.6)	1.7 \div 2 (0.6 \div 0.5)	3.3 \div 5 (0.3 \div 0.2)	—
Amorphous (brittle)	1.25 \div 1.5 (0.8 \div 0.65)	1.5 \div 2 (0.65 \div 0.5)	2 \div 2.5 (0.5 \div 0.4)	—	5 \div 6.2 (0.2 \div 0.16)
Glass fiber-reinforced	1.4 \div 1.8 (0.7 \div 0.55)	1.8 \div 2.2 (0.55 \div 0.45)	2.2 \div 2.9 (0.45 \div 0.35)	4 (0.25)	6 (0.17)

(R' factors in parentheses; $R = 1/R'$)

Table 1.25 Estimation of R factors for various types of thermoplastics [105]

For the determination of the safety factor S there are number of aspects that are only remotely material-dependent [106]:

- Safety factors for technically important applications are defined in design specifications, guidelines, standards, or company data sheets by the consensus of recognized experts based on previous experience and investigation results.
- Despite identical load conditions, safety regulations can be different in different countries.
- Aspects of over-dimensioning take into consideration danger to living beings and objects due to failure.
- The more precisely service load can be predicted, the lower the safety factors.

- The more reliable and precise the calculation methods are, and the more reliably material behavior can be evaluated, the lower the safety factor is set.
- Failure evaluations considering instability have to be performed with increased safety coefficients, because slight deviations from reference geometry and intended force introduction can lead to excess load conditions
 - When loading conditions are inhomogeneous, a modified, usually increased safety coefficient has to be used with materials characteristic data acquired under homogeneous stress distribution.
 - For plastics parts prone to creep and environmental influences, increased safety factors in addition to materials-dependent reduction factors need to be applied.
 - Semi-crystalline thermoplastics can be assigned lower safety factors than amorphous thermoplastics, thermosets or fiber-reinforced plastics, owing to their ductile material behavior.
 - Safety factors have to be adapted to technological progress, production technology, materials quality, calculation feasibility, experience, knowledge of loading conditions, etc.
 - When plastics property changes caused by aging, chemical influence, water absorption, and heat influence cannot be specified in the R factors, they have to be reflected in the safety factors.

1.6.3.1.2 Failure Criteria

Most technical parts are loaded by a multi-axial stress state caused by external loads acting on them. Whether this stress state leads to failure is judged using a suitable failure criterion – also known as a fracture-criterion or -hypothesis. With such a mathematical formulation of all possible stress states leading to failure, a multi-axial stress state is reduced to a comparative stress σ_c by which the material is assumed to be loaded [107].

In this way, hard-to-measure shear resistance can be determined rather precisely by the mathematically simple *shear stress criterion*:

$$\sigma_f = \sigma_1 - \sigma_2 \quad (1.46)$$

Consequently for *shear resistance* τ_s :

$$\tau_s = 0.5 \cdot \sigma_f \quad (1.47)$$

For plastics with different tensile σ_{tS} and compression strengths σ_{cS} ,

$$\tau_s = \frac{m}{m+1} \cdot \sigma_{tS} \quad \text{with} \quad m = \frac{\sigma_{cS}}{\sigma_{tS}} \quad (1.48)$$

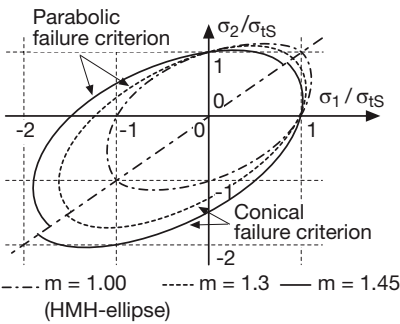
Moreover, experience shows that the **HMH criterion** (criterion of greatest shape deformation work according to Huber, von Mises and Henky) also usually provides sufficiently precise results. Then comparative stress is:

$$\sigma_{cHMH} = \frac{1}{\sqrt{2}} \cdot \sqrt{(\sigma_1 - \sigma_2)^2 + (\sigma_3 - \sigma_1)^2 + (\sigma_2 - \sigma_3)^2} \tag{1.49}$$

For shear resistance it follows that:

$$\tau_s = 0.58 \cdot \sigma_s \tag{1.50}$$

Brittle and stress-cracking sensitive plastics in particular are rated too high by this hypothesis in the biaxial tensile range, whereas data obtained in the compressive region are generally conservative. Plastics whose compression strength σ_{iS} is higher than their tensile strength σ_{cS} are thus better evaluated using the conical or parabolic failure criterion, Figure 1.53. Alternatively, their shear resistance may be calculated using tensile strength for practical purposes. In these criteria, failure occurs in a triaxial stress state when the 3-dimensional cone or paraboloid is punctured internally, Figure 1.54. Both are symmetric to the space diagonal $\sigma_1 = \sigma_2 = \sigma_3$ and characterized by the fact that failure occurs under multiaxial tensile loading, but infinite strength is obtained under general compression load. If the cone or paraboloid is truncated in a two-dimensional load plane, ellipses result that characterize biaxial load conditions, Figure 1.53.



Ductile			Brittle		
Material	σ_{iS} [N/mm ²]	m	Material	σ_{iS} [N/mm ²]	m
PS	73	1.33	PMMA	59	1.40
PVC	54	1.30	CAB	34	0.91
PC	59	1.22	CA	41	1.23
PE	11	1.34	PVCA	66	1.29
PP	32	1.32	EP	81	1.45
PA	66	0.92			
ABS	44.5	0.95			

Figure 1.53 Comparison of experimental failure curves and failure curves calculated according to conical and parabolic failure criteria in the diagram of main planar stress ($m = \sigma_{cS} / \sigma_{iS}$, $m = 1$ isotropy) [107, 108]

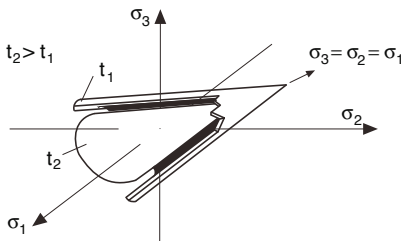


Figure 1.54 Three-dimensional failure diagrams interposed to consider the influence of time on the strength of plastics. Load duration to failure $t_1 < t_2$ [107]

Conical failure criterion:

$$\sigma_{con} = \frac{m-1}{2 \cdot m} (\sigma_1 + \sigma_2 + \sigma_3) \pm \frac{1+m}{2 \cdot \sqrt{2}} \cdot \sqrt{(\sigma_1 - \sigma_2)^2 + (\sigma_3 - \sigma_1)^2 + (\sigma_2 - \sigma_3)^2} \quad (1.51)$$

Parabolic failure criterion:

$$\sigma_{par} = \frac{m-1}{2 \cdot m} (\sigma_1 + \sigma_2 + \sigma_3) \pm \frac{(1+m)^2}{4 \cdot m^2} \cdot \sqrt{(\sigma_1 + \sigma_2 + \sigma_3)^2 + \frac{1}{2 \cdot m} [(\sigma_1 - \sigma_2)^2 + (\sigma_3 - \sigma_1)^2 + (\sigma_2 - \sigma_3)^2]} \quad (1.52)$$

These criteria are often inadequate for anisotropic materials such as fiber-composite plastics or plastics that have become strongly anisotropic due to processing orientation, because their properties vary strongly parallel and perpendicular to orientation as well as under compression and tension.

Time-dependent failure behavior can be visualized as interposed 3-dimensional failure diagrams (Figure 1.54), where the outer body exhibits higher creep resistance due to its shorter loading time. Actual measurement results are not available.

1.6.3.1.3 Strain-Related Dimensioning

Conventional failure considerations have neglected strain-related dimensioning for the obvious reason that failure caused by large deformations is rare for most components, especially machine elements made from metals. Plastics, however, exhibit low stiffness due to the structure of their macromolecules and intermolecular, physical bond forces. Their stiffness is often less than 1/100 of steel, while their strength is only 1/10 of steel.

The stress-strain behavior of plastics stands out because at variable loading rates (and/or time, and/or temperature), the stress at the yield point changes to a higher degree – by as much as the tenth power – than the accompanying ultimate strain. Tensile strain in many plastics is largely independent of time and temperature and amounts to ca. 5%, while changes in stress can amount to one order of magnitude. That means that for components made from plastics, deformation consideration and testing by measuring deformation play a much greater role than for metals.

Another dimensioning limit (verified only empirically) is critical strain according to Menges, which characterizes the occurrence of the first relevant irreversible degradation in plastics [109, 110].

For short-glass fiber- reinforced plastics, the following approximation holds:

$$\varepsilon_{crit.GF} \sim \varepsilon_{crit} \cdot (1 - 1.5 \psi^2) \quad (1.53)$$

with ψ = Weight proportion of glass fibers

Dimensioning with critical strain encourages the designer to think in terms of strain and allows for a first, tentative design of a component.

Plastics	Critical strain
Amorphous, unfilled thermoplastics, exception: polystyrene	0.8% 0.2%
Semi-crystalline thermoplastics (above T_g , otherwise see amorphous thermoplastics)	2.0%
Impact modified blends	0.8%
UP resin laminates	0.25%
VE resin laminates	0.27%

Table 1.26 Critical strain in plastics

Proof of ultimate strain for containers, especially for fiber reinforced plastics, should be shown as follows:

$$\varepsilon_{exist} = \frac{\sigma_{exist} \cdot R_{1Y}}{1.1 \cdot E_{5/75}} \quad (1.54)$$

with R_{1Y} = reduction factor to allow for load duration up to 20 years for instability (see Table 1.31)

$E_{5/75}$ = 5% fractile of the Young's modulus at 75% confidence factor

For load bearing laminates, the ultimate strains provided in Table 1.27 can be applied, if the media-loaded side consists of a random fiber layer of approx. 450 g/m², has a protective chemical layer, or a liner.

Resin type of load bearing laminate				Medium
EP resins	UP resins 1110 - 1140	PHA resins 1330 1310		
0.5%	0.5%	0.6%	0.65%	Media list 40-2.1.1 - 2.1.3 except group IV and H ₂ SO ₄
0.25%	0.25%	0.25%	0.25%	Media list 40-2.1.1 - 2.1.3 except group IV and H ₂ SO ₄

Table 1.27 Ultimate strains of laminates [7]

It is not necessary to prove ultimate strain for the side not loaded by the medium, if the load bearing laminate has a random-fiber surface layer with approx. 450 g/m².

Liner	Ultimate strain ϵ_{ult}
PVC – normal impact resistant	0.25%
PVC – highly impact resistant	0.40%
PP	0.50%
PVDF	0.50%

Table 1.28
Ultimate strains of thermoplastic liners

It should be noted that the stresses in components are typically measured with strain gauges from which the loads still have to be calculated. Despite this fact, strain-related failure criteria are only occasionally applied to very brittle plastics.

1.6.3.1.4 Number Test Specimens – Probabilistic

As in every test, the results from mechanical properties tests on composite materials depend on chance variations in a number of influencing factors. The stochastic character of measurement results requires the use of statistical evaluation methods [15].

Tests for a particular property generally aim at determining the average value of the population mean (true average) and standard deviation from the population mean (true standard deviation). To do so, all elements of the population would have to be tested, which makes no sense, because subsequently all components would be destroyed. Thus, usually only a limited number of measurements are performed. From previous experience and experimental investigations with composite materials, it is known that measurements of elasticity characteristics are less scattered than those of strength characteristics. Scatter also increases in the order: unidirectional < fabric- < mat-reinforced composite materials.

Of late, lower limit values, so-called fractile values, are being recorded in probabilistic considerations in order to determine material characteristic data, because the frequently wide scatter in measured values and load data no longer permit calculation of characteristic values using average values.

In order to allow for the random character of loads on the one hand and characteristic data on the other, deviations have to be considered.

It is quite possible that the scatter zones of load and loadability overlap, Figure 1.55. The degree of overlap represents a measure for a particular failure probability. In the hatched area, the requirement of $\sigma_{exist} < \sigma_{adm}$ is no longer fulfilled under strength-related consideration. This case can be avoided by selecting suitable one-sided limit values by determining an upper limit value on the characteristic side.

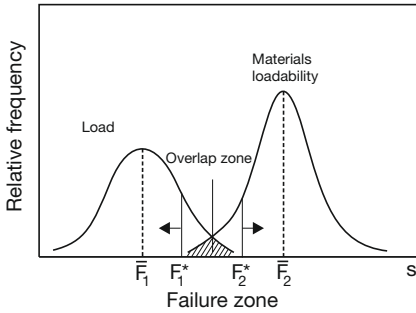


Figure 1.55

Overlap in distribution functions of load and material loadability; \bar{F} = average value, F^* = fractile value

By comparing an upper limit value F_1^* with a lower limit value F_2^* , all deviations from median values are considered. If F_1^* is considered as the resistance fractile and F_2^* as the effective fractile, then a nominal measure of safety can be formed as the quotient of the resistance and effective fractiles.

A fractile value F_ε^* characterizes a certain characteristic value below or above which only a certain percentage ε of all measured values are found. Such a fractile value can, however, be stated only with a certain confidence factor or degree of confidence W , because the fractile value is determined by only a limited amount of information. The fractile value can be formulated as follows:

$$F_\varepsilon^* (\%) = \bar{x} \pm k \cdot s \quad (1.55)$$

The fractile value $F_\varepsilon^* (\%)$ is calculated from the average value \bar{x} of a measurement series plus/minus the product of standard deviation s and the k -factor with

$$k = f(n, \varepsilon, W) \quad (1.56)$$

Calculating with fractile values presumes precise knowledge of data distribution. If the measured data exhibit normal, i.e., Gaussian, distribution, then the k -factor is calculated from Student's t -distribution, Table 1.29. Tensile strength values and flexural strength data exhibit mainly Gaussian distributions; Young's moduli and time-dependent values exhibit logarithmic normal distributions, Figure 1.56. In both cases, the fractile value is a function of random sample size n , of a lower limit ε , and a confidence factor W .

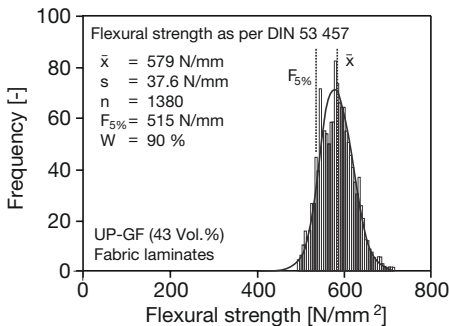


Figure 1.56

Distribution of 1,380 flexural strength measurements of a 64 wt.% UP-GF glass fiber-woven laminate

n	5	6	7	8	9	10	11	12	13	14	15	30
k_s (75%)	2.46	2.34	2.25	2.19	2.14	2.10	2.07	2.05	2.03	2.01	1.99	1.65
k_s (90%)	3.40	3.09	2.89	2.85	2.67	2.57	2.50	2.45	2.40	2.36	2.33	2.08
k_s (95%)	4.20	3.94	3.55	3.30	3.11	2.98	2.86	2.78	2.70	2.65	2.59	2.23

Table 1.29 k -factors as a function of the number n of values measured at 75%, 90% and 95% confidence factor

In engineering practice, calculation is usually done with a lower limit $\varepsilon = 5\%$ and a confidence factor $75\% \leq W \leq 95\%$. At determined limit ε and confidence factor W , the fractile value is only a function of the sample size n . For a 5% fractile lower limit value with a confidence factor $W = 95\%$, a number of samples $n = 10$ represents a meaningful quantity. Precision is of course higher at $n = 20$, Figure 1.57, resulting in a higher value for assumed strength. In case no statistical information is available, $n = 30$ should be aimed for, depending on the shape of the specimen.

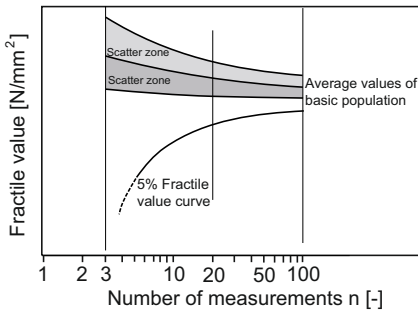


Figure 1.57 Schematic curve of fractile value $F5\%$ as a function of sample size n

1.6.3.1.5 Reduction Factors for Load-Bearing Plastics Parts

The most detailed recommendations for the configuration of load bearing plastics parts apply to fiber-composite designs, especially when they are subject to official technical approval [7, 110, 111, 112, 113].

The most frequently used materials data for short-term loading are those for Young's modulus and ultimate strain. Allowances for reductions include A_1 for duration of acting load, A_2 for media influence incl. weathering, moisture, chemicals, and A_3 for temperature. Various factors are selected that correspond with the material data, so that, in addition to reductions in terms of load, strength, stiffness (stability) and deformability (strain limit), distinctions are made for environmental influences and load duration, e. g., A_{1F} for reduction due to load duration until fracture, A_{1V} for stability, and A_{1U} ultimate strength.

Reference values for unreinforced plastics are empirical data whose validity has to be demonstrated, Table 1.30.

	Unreinforced							
	Thermoplastics					Thermosets		
	PP-H	PVC-NI	PVDF	PMMA	PE 80	UP	EP	PUR
Loading duration up to 20 years								
A _{1S} (strength)	2.0 ⁽⁴⁾	1.9 ⁽⁴⁾	1.2 ⁽⁴⁾	2.3 ⁽¹¹⁾	pressure: 1.5 ⁽⁶⁾ tensile: 1.7 ⁽⁶⁾	1.6 ⁽⁸⁾	1.5 ⁽⁸⁾	2.1 ⁽¹⁰⁾
A _{1Y} (Young's modulus)	5.8 ⁽³⁾	1.9 ⁽³⁾	1.1 ⁽⁴⁾	2.5 ⁽⁸⁾	4.7 ⁽³⁾	1.7 ⁽⁸⁾	2.0 ⁽⁸⁾	shear: 4.4 ⁽¹⁰⁾ pressure: 3.4 ⁽¹⁰⁾
R _{1Y} (ultimate strain)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0 ⁽¹⁰⁾
Media influence								
A _{1S} (strength)	1.1 ⁽⁵⁾	1.0 ⁽⁵⁾	– ⁽⁹⁾	– ⁽⁹⁾	pressure: 1.0 ⁽⁶⁾ tensile: 1.1 ⁽⁶⁾	– ⁽⁹⁾	– ⁽⁹⁾	1.2 ⁽¹⁰⁾
A _{1Y} (Young's modulus)	1.1 ⁽¹⁾	1.4 ⁽¹⁾	– ⁽⁹⁾	– ⁽⁹⁾	1.1	– ⁽⁹⁾	– ⁽⁹⁾	1.2 ⁽¹⁰⁾
R _{1Y} (ultimate strain)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0 ⁽¹⁰⁾
Temperature influence up to 40 °C								
A _{1S} (strength)	1.3 ⁽⁴⁾	1.6 ⁽⁴⁾	1.2 ⁽⁴⁾	1.3 ⁽¹¹⁾	1.4 ⁽⁶⁾	– ⁽⁹⁾	– ⁽⁹⁾	1.1 ⁽¹⁰⁾
A _{1Y} (Young's modulus)	1.2 ⁽²⁾	1.3 ⁽²⁾	1.5 ⁽⁴⁾	1.2 ⁽¹¹⁾	1.3 ⁽¹⁾	– ⁽⁹⁾	– ⁽⁹⁾	1.1 ⁽¹⁰⁾
R _{1Y} (ultimate strain)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0 ⁽¹⁰⁾

⁽¹⁾: DIN 4266-1. Table 1. Seepage pipes for landfills

⁽²⁾: DIN 4266-1. Table 2. Seepage pipes for landfills

⁽³⁾: "Mitteilungen" of the DIBt 1995. page 146

⁽⁴⁾: DIN EN 1778 Characteristic values for thermoplastics designs

⁽⁵⁾: DIN EN 1778 Table A1 (reduction factors for media influence)

⁽⁶⁾: DIBt: Provisional dimensioning principles for parts in landfills

⁽⁷⁾: DVS 2205-1. section 10

⁽⁸⁾: Long-term deformation behavior of plastics materials, Institut für Leichtbau und ökonomische Verwendung von Werkstoffen, Dresden, Schriftenreihe "Materialökonomie", Heft 32

⁽⁹⁾: No data available, tests required

⁽¹⁰⁾: See literature list in the guideline

⁽¹¹⁾: U. Gleiter, Use of transparent thermoplastics in building construction, Dissertation, TU Darmstadt, 2002

Table 1.30 Reduction factors considering loading durations up to 20 years (top), of media influences (center), and temperature influence to 40 °C [111]

With glass fiber-reinforced reaction resins, practically any kind of glass fiber product structure is possible. It is hard to provide general standards for reduction. Thus it was attempted to define standard laminates and provide standards for typical structures made from various types of resins and various glass fiber contents. A compilation can be found in DIN 18820 (1991) [8]. Section 1 compiles the structure, manufacture and properties of laminates from six different specified types of glass fiber-reinforced UP and PHA resins. Section 2 characterizes the types of reinforcements and their structures; it also lists reference values for Young's modulus and strength as well as additional reduction factors for various operating temperatures. Section 3 recommends reduction factors for various chemicals and recommends resins from Section 1 for such applications. Section 4 deals with testing and monitoring. The data given in Table 1.31 are recommended as strength reduction factors for up to 20 years of loading, taking into consideration the various resin types according to DIN 18820-1. Here, no distinction is made between the load types such as normal force and flexural load, nor is the degree of curing considered as is the case for reduction factors for stability (Young's modulus) and ultimate strain in Table 1.32, since resistance is more strongly dependent on the degree of curing.

Types of material (DIN 18820-2)	R_{1S}
Random oriented fiber laminates (mat)	1.6
Mixed laminates (mat/non-woven)	$2.0 - \psi^{(1)}$
Wound laminates (rovings in direction of circumference/mat) parallel to direction of winding	$1.8 - \psi^{(1)}$
Wound laminates (rovings in direction of circumference/mat) perpendicular to direction of winding	$1.7 \div 2.75^{(2)}$
With ultimate strain $\varepsilon_t^{(3)} > 0.2\%$	$2.1 \div 3.9^{(3)}$
Wound laminates (mat, rovings in direction of circumference, unidirectional non-woven) parallel to direction of winding	$1.8 - \psi^{(1)}$
Wound laminates (mat, rovings in direction of circumference, unidirectional non-woven) perpendicular to direction of winding	$1.6 \div 1.9$
Pultrusion profiles parallel to direction of pultrusion	$1.2 \div 2.0 (\varepsilon_t > 0.2\%)$
Pultrusion profiles perpendicular to direction of pultrusion	$2.0 \div 3.0 (\varepsilon_t > 0.2\%)$

⁽¹⁾: ψ = glass fiber weight content

⁽²⁾: Fiber structure depending on resin type [8]

⁽³⁾: ε_t strain under tensile loading perpendicular to direction of winding

Table 1.31 Reduction factor for strength R_{1S} for GF-UP and GF-VE (for more precise information on structure see DIN 18820, Part 2; [8])

Type of material	R_{1Y}	;	R_{1U}
Random oriented fiber laminates (mat)	Annealed $2.4 - 2 \delta$		Non-annealed $2.6 - 2 \psi$
Mixed laminates (mat/non-woven)	Annealed $2.3 - 2 \delta$		Non-annealed $2.5 - 2 \psi$
Wound laminates (rovings in circumference direction/ mat) parallel to direction of winding	Normal force $1.75 - \psi$		Bending $1.85 - \psi$
Wound laminates (rovings in circumference direction/ mat) perpendicular to direction of winding	$2.2 \div 3 - \psi$ or $3.2 - 2 \psi$		
With limit strain $\varepsilon_t^{(3)} > 0.2\%$	$2.6 \div 4 - \psi$ or $4.0 - 2 \psi$		
Wound laminates (mat, roving in circumference direction, unidirectional non-woven) parallel to direction of winding	Normal force $1.75 - \psi$		Bending $1.85 - \psi$
Wound laminates (mat, roving in circumference direction, unidirectional non-woven) perpendicular to direction of winding	$1.8 - \psi / 2) \div (2.3 - \psi)$		
Pultrusion profiles parallel to pultrusion direction	Normal force $1.1 \div 1.4 (\varepsilon_t > 0.2\%)$		Bending $1.2 \div 1.6 (\varepsilon_t > 0.2\%)$
Pultrusion profiles perpendicular to pultrusion direction	Normal force $1.5 \div 2.0 (\varepsilon_t > 0.2\%)$		Bending $1.8 \div 2.5 (\varepsilon_t > 0.2\%)$

⁽¹⁾: ψ = glass fiber weight content

⁽²⁾: Fiber structure depending on resin type [8]

⁽³⁾: ε_t strain under tensile loading perpendicular to direction of winding

Table 1.32 Reduction factor for stiffness (Young's modulus) R_{1Y} and limit strain R_{1U} due to loading duration to 20 years for GF-UP and GF-VE

In cases of media influence distinguishes between liquids with very little or moderate influence on laminates, as well as aggressive media in gaseous or liquid form that come in contact with laminates. Reduction factors are compiled in Table 1.33 [8].

Media class according to DIN 18820-3	Annealed	Non-annealed	
No influence	1.0	1.0	Dry, interior
Very little influence	1.1	1.2	Very little influence
			Natural weathering < 30 °C
Little influence	1.2	1.3	Natural weathering in ground 30 to 40 °C
			In buildings or in the open < 30 °C
			In buildings or in the open: 30 to 40 °C
	1.3	1.4	

Table 1.33 Reduction factors for strength, stiffness (Young's modulus) and ultimate strain under media contact for GF-UP and GF-VE

For media with little influence, a fine or non-woven layer is considered sufficient surface protection, while for aggressive media, a chemical protective layer has to be provided that is not part of the load bearing laminate.

For the selection of resins for the chemical protective layer, a distinction is made between outdoor loads at operating temperatures up to 30 °C and operating temperatures between 30 °C and 40 °C. Recommendations are made for inorganic bases and their basic hydrolyzed salts, for inorganic, oxidizing bases and their basic hydrolyzing salts, for inorganic acids and their acid hydrolyzing salts, for inorganic, oxidizing acids and their acid hydrolyzing salts, for organic bases (e. g., amines), for organic acids, for detergents and additives, for plasticizers and solvents, for other oxidation agents and for other media (ϵ -caprolactam).

Reduction factors for the influence of operating temperature are compiled in Table 1.34.

Temperature range	$A_{3B, E, D}$	Conditions
- 20 °C to 30 °C	1.0	Parts in the ground, in the open, in buildings and up to an operating temperature of 30 °C
> 30 °C to 40 °C	1.6 - ψ	Operating temperature
> 40 °C to 60 °C	1.8 - ψ	Operating temperature

Table 1.34 Reduction factors for temperature influence, ψ glass fiber weight content for GF-UP and GF-VE

1.6.3.2 Service Life for Technical Parts Under Mainly Static Loads

1.6.3.2.1 Acquiring Permissible Load

As a rule, all technical components are dimensioned such that their expected service life is longer than the lifetime for which they are to be warranted. This is also true for each individual part, unless originally configured to be a wear part and characterized as such. All aspects of a particular load must be taken into consideration: type, duration, temperature, media exposure, processing and post-processing operations.

Despite the progress made in computer-aided treatment of structure-property relationships, dimensioning under such complex conditions continues to depend on experimental results obtained in creep investigations, S-N diagrams, as well as media and weathering investigations.

Figure 1.58 provides long-term characterization for plastics in engineering applications, considering the influences of mechanical and thermal load and media exposure during use that usually occur simultaneously.

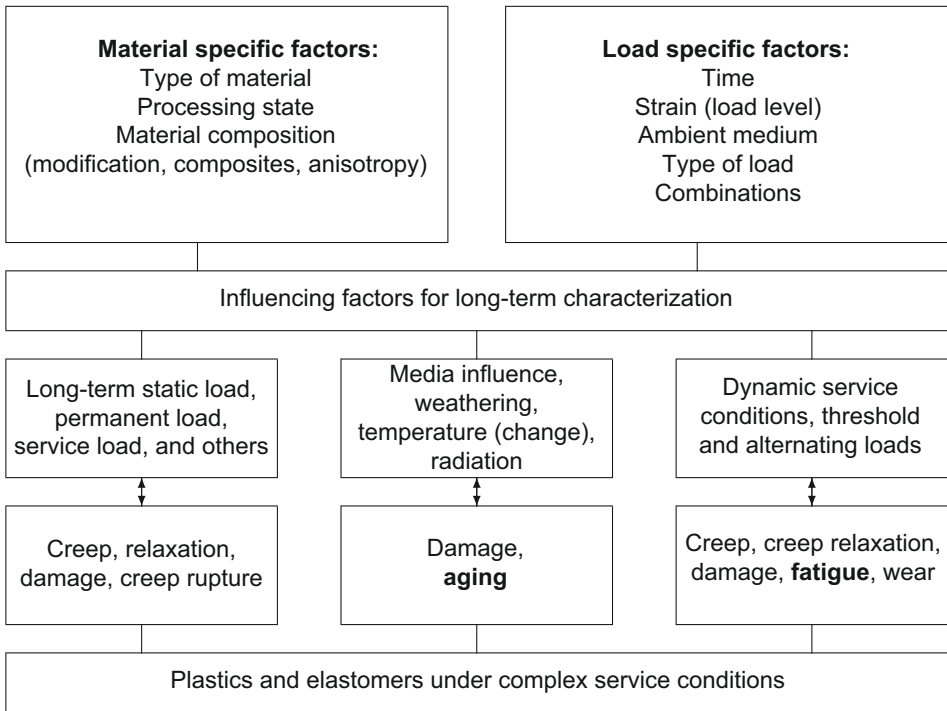


Figure 1.58 *Resistance and aging in plastics – long-term reliability*

Aging in this context generally refers to the wider sense of the word, i. e., it includes simultaneous effects of long-term static and/or dynamic load. Figure 1.59 left shows typical curves for a creep diagram. For a defined material, time t , and thermal/medial load, the corresponding tensile stress at break can be determined with a certain degree of uncertainty. Because an infinite number of creep curves is possible (depending on processing state and load), we refer to imaginary curve segments. With increasing service life the indicators for aging, such as loss in strength and impact resistance, embrittlement, etc., also increase, so that the extrapolation of such creep curves has limitations. One way to circumvent these limitations is to use schematic diagrams showing aging limit (t_2). For actually investigated materials (Figure 1.59 right), the curves end in conjunction with the test parameters, with the result, that there is always a data pair of maximum stress and corresponding life expectancy for any given point of intersection. Any prognostication of the aging behavior of newly developed materials, blends or composites begins with time-compressing load simulations and requires long-term subsequent testing.

ISO 9080 [114] describes a standard extrapolation method, abbreviated SEM, for predicting the service life creep behavior of pipes. The SEM method involves internal pressure tests at two or more temperatures, linear regression analysis with an estimation of regression quality, curve fitting and three different ways of expressing bend in hydrostatic pressure measurement.

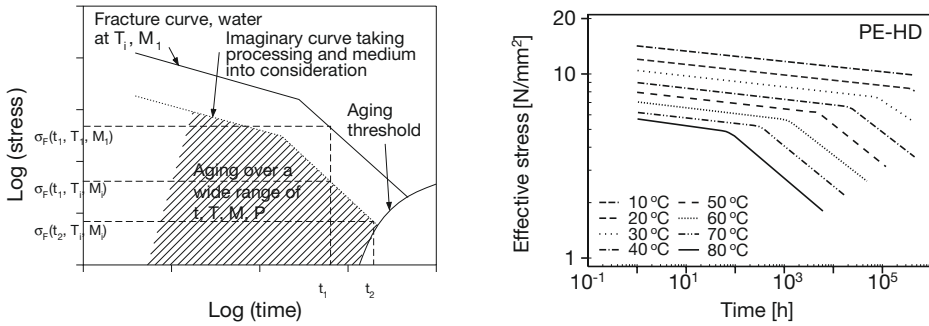


Figure 1.59 Creep diagram

Left: service life determination under certain materials and operating conditions
(t = time, T = temperature, M = medium, P = processing)

Right: results from internal pressure creep tests with PE-HD pipes according to DIN 16887

The transition from measured data to parameters suitable for dimensioning/calculation is achieved by including a safety factor according to Eq. 1.57:

$$Y_{adm} = \frac{Y_0(t_Y, M_Y, T_Y, V_Y)}{S_Y}; \quad \sigma_{adm} = \frac{\sigma_0(t_Y, M_Y, T_Y, V_Y)}{S_\sigma}; \quad \varepsilon_{adm} = \frac{\varepsilon_{crit}}{S_\varepsilon} \quad (1.57)$$

- with
- Y_{adm} = admissible Young's modulus
 - Y_0 = Young's modulus measured under operating conditions
 - t_Y = service time
 - M_Y = medium
 - U_Y = ambience (climate, humidity) during operation
 - T_Y = service temperature
 - V_Y = processing method
 - S_Y = safety factor corresponding to parts function and dimensioning
 - S_σ, S_ε = method
 - σ_{adm} = admissible stress
 - σ_F = tensile stress at break for particular load case (tensile, compression)
 - ε_{adm} = admissible strain
 - ε_{crit} = critical strain

The safety factors S represent estimates and empirical values and thus reflect to a certain extent the uncertainties regarding the history of both material and load [8]. Table 1.35 offers an insight. (The probabilistic or semi-probabilistic calculation method with boundary conditions enables a reduction to system-dependent safety factors [115]. However, considerable statistical effort is required to secure each individual dimensioning factor.)

Design group	Resistance against			
	Fracture	Inadmissible deformation	Inadmissible strain	
			Strength calculation	Rigidity calculation
Molded parts in general	1.1 to 1.5	1.0 to 1.5	1.1	1.5
Functional parts	1.5 to 1.8	1.8 to 2.0	1.2	1.7
Functionally critical parts	1.8 to 2.7	2.5 to 3.0	1.3 to 2.0	

Table 1.35 Suggestions for selecting safety factors

If designers do not have materials data available fitting their case of application, specific reduction factors $A_{1,2,\dots,n}$ according to Eq. 1.58 may be utilized.

$$\sigma_{adm} = \frac{\sigma_F(t_0, U_A, T_R, P_0)}{S_o \cdot A_1 \cdot A_2 \cdot A_3 \cdot A_4} = \frac{\sigma_F(t_0, U_A, T_R, P_0)}{S_o} \cdot \prod A_i \quad (1.58)$$

- with t_0 = short-term load
 U_A = ambient medium air
 T_R = room temperature
 P_0 = standard processing
 A_1 = reduction factor for long-term use
 A_2 = reduction factor for special medium
 A_3 = reduction factor for increased service temperature
 A_4 = reduction factor for special processing

The reduction of short-term characteristics determined at normal temperature and in air as the ambient medium, occurs multiplicatively over time, temperature, media, and processing influence.

Reduction factor A_1 considers the influence of time, e.g., depending on the actual behavior of the characteristic property; $A_1 = 1.8$ for loads lasting up to 104 h and $A_1 = 2$ for long-term static load lasting for more than 105 h.

Reduction factor A_2 considers media contact, e.g., in containers the influence of the storage medium on the load bearing laminate. Because the medium comes in contact with the load bearing laminate only if the protective chemical layer fails, i.e., only in case of leakage, $A_2 = 1.1$ is used as a safety factor up to operating temperatures of 60 °C. For coatings, protective chemical layers or liners, A_2 alone is valid because they are not load bearing. For parts subject to official approval, A_2 and A_3 values are listed in the appendix.

Reduction factor A_3 considers the influence of storage medium temperature on a load bearing layer. In strength calculations, it is valid for fracture (F) as well instability (I):

- operating temperature < 40 °C: $A_{3F} = A_{3I} = 1.05$
- operating temperature < 60 °C: $A_{3F} = A_{3I} = 1.15$

Reduction factor R_4 considers damage to the base material due to processing and joining technology. This also covers variations in the degree of cure, reinforcing and filler content, as well as orientation. Table 1.36 shows how reduction factors $R_{1,2,3,4}$ are selected for a particular part and material under specific service conditions, when only short-term mechanical data are available for dimensioning. Each reduction factor implies a ratio of virgin plastics under short-term load, room temperature and ambient air to the processed plastic at the time of corresponding operating conditions, Eq. 1.59:

$$R_1 = \frac{\sigma_f(t_0, M_Y, T_Y, V_Y)}{t_Y, M_Y, T_Y, V_Y}; \quad R_2 = \frac{\sigma_f(t_Y, M_L, T_Y, V_Y)}{t_Y, M_Y, T_Y, V_Y}; \quad (1.59)$$

$$R_3 = \frac{\sigma_f(t_Y, M_Y, T_R, V_Y)}{t_Y, M_Y, T_Y, V_Y}; \quad R_4 = \frac{\sigma_f(t_Y, M_Y, T_Y, V_O)}{t_Y, M_Y, T_Y, V_Y}$$

with R = reduction factor(s)
 i = 1 to n

Component part		Reduction factors								
		Fracture				Instability				
		R_{1F}	R_{2F}	R_{3F}		R_{1I}	R_{2I}	R_{3I}	R_4	
		< 30 °C	< 40 °C		< 30 °C	< 40 °C				
Mixed laminate floor		1.8 1.5	1.1	1.1	1.15	1.7 1.4	1.1	1.15	1.2	
Cylinder wound laminate	Direction of circumference	1.9	1.1	1.1	1.15	1.5	1.1	1.1	1.15	1.1
		1.55				1.3				
	Axial direction	2.1	1.1	1.1	1.15	1.9	1.1	1.1	1.15	1.1
		1.65				1.55				
Overlay		2.0	1.1	1.1	1.15	1.9	1.1	1.1	1.15	1.3
Random oriented fiber laminate		1.6				1.55				

A_i considers time influence: value at top applies for $2 \cdot 10^5$ h, value at bottom applies for $2 \cdot 10^3$ h

Table 1.36 Examples for determining reduction factors for supporting parts on a flat-bottom container made from GF-UP (with liner)

Time influence R_{1F}	10 ⁰ h			10 ³ h			10 ⁴ h		
Temperature influence R_{3F}	PP	PVC-H	GFK-MD	PP	PVC-H	GFK-MD	PP	PVC-H	GFK-MD
23 °C	1.0	1.0	1.0	2.0	1.1	1.3	2.4	1.3	1.4
40 °C	1.4	1.2	1.1	2.6	1.6	1.4	3.0	2.4	1.5
60 °C	1.9	1.4	1.6	3.6	2.6	2.0	4.1	9.7	2.1

Table 1.37 Multiplicative influence of time and temperature on reduction factors by $R_{1F} \times R_{3F}$ in thermoplastic and thermoset applications; reference parameter is tensile strength under short-term load at normal temperature

If sufficient results are known from correspondingly complex long-term investigations, such data are utilized, and $R_{tot} = R_1 R_2 R_3 R_4 = 1$, see Eq. 1.57. To this extent, data banks and complex data functions are not only elegant, but necessary aids for selecting materials and dimensioning components [116]. Table 1.37 shows the strong differentiation between time and temperature degradation R_1 and R_3 for the three classic container plastics PP, PVC, and GFK, thus emphasizing the poor informational value of short-term data. It is advised to perform at least triparametric investigations, e. g., for strength as a function of time, temperature and medium, or, as in Figure 1.60, for strength, temperature, and media absorption.

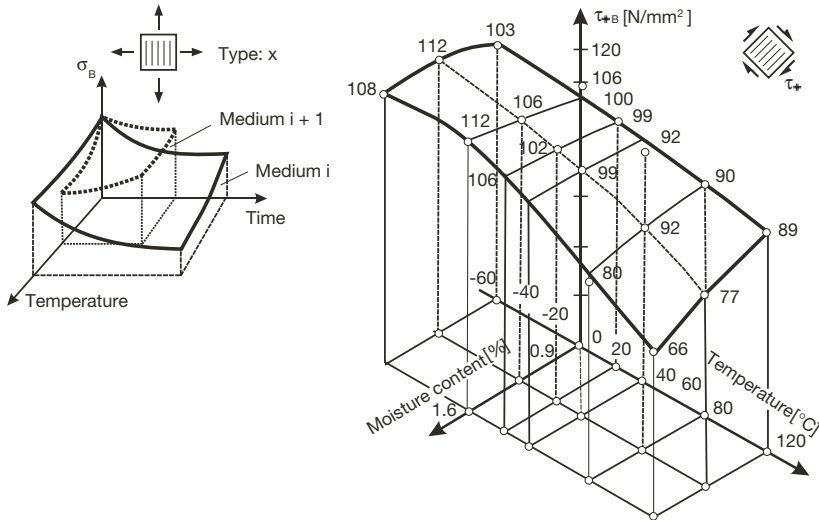


Figure 1.60 Recommended multiparametric representations of dimensioning characteristics for a design calculation

1.6.3.2.2 Determining Existing Loads

The dimensioning of plastics components for defined operating times and corresponding service life has to fulfill strict requirements. Components made from unreinforced plastics exhibit viscoelasticity, physical and geometric non-linearity. In reinforced plastics, viscosity is less critical, but inhomogeneity, layer sequence and anisotropy become relevant. The exact determination of these characteristics is always a very complicated mathematical task.

In practical design cases:

- stiffness data are calculated using programs for linear elastic materials, including the Young's modulus corresponding to the particular service time conditions, load level, and environment.
- strength data are acquired using the theory of elasticity to determine stress values, while durability is ensured by the resistance of the materials to be selected.