

Long-Term Behaviour of Thermoplastic Materials

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Content:

- 1. Basics**
- 2. Autooxidation**
- 3. Chemical Resistance**
- 4. Biodegradation**
- 5. Extrapolation of the Lifetime by Accelerated Ageing Tests**

1. Basics

Polymer materials do find increasingly access in products with a lifetime of a few years up to several decades. Newer material and compound developments achieve technical material-properties (e.g. tensile strength) like those of metals and ceramics, and provide a number of advantages compared to the materials approved over centuries (e.g. moulding, weight saving, impact-strength, ...). Though many polymers are subject to some changes of physical (e.g. changing of the morphology) and chemical provenience (e.g. oxidation) during processing and service, nowadays it is possible to adjust specific requirements in regard to life expectancy by suitable modification (e.g. co-polymerisation, additives).

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Table 1 gives an overview on the common thermoplastic materials and their long-term applications.

Table 1: Long-term application of thermoplastic materials

Abbr.	Name	Samples for long-term application
PE	polyethylene	electrical cable insulation
PP	polypropylene	functional parts in washing machines
PB	polybutene	hot water tubes (floor heating)
PS	polystyrene	thermal insulation (facade construction with EPS)
ABS	acrylnitrile-butadiene-styrene-terpolymer	jackets of household devices and computers, crash helmets and car construction
PMMA	polymethyl-methacrylate	glass substitute
PVC-U	unplasticized polyvinyl chloride	water tubes (also underground), windows
PVC-P	plasticised polyvinyl chloride	electric cable-insulation; foils (roof, tunnel, floor, ...); profiles (window sealing)
POM	polyoxymethylene	vehicle construction (ca. 5kg / vehicle), household devices
PA	polyamide	electro techniques + electronics, vehicle construction
PBT	polybutylene-terephthalate	vehicle construction
PC	polycarbonate	glass substitute, electro techniques (casing)
PUR	polyurethane (TPU, PU-foams ...)	shoe soles (TPU), vehicle construction (cushioning)
FP	fluor containing polymers (PTFE, FEP, PFA, ETFE, PVDF, ...)	chemical engineering

The requirements on long-term products are versatile and have to be defined before developing. Figure 1 summarizes the relevant stresses. Normally some of the mentioned stresses occur at the same time or by turns, which complicate an exact definition of the requirements as well as the stress simulation tests of the chosen material.

The most relevant stresses / stress combinations for long-term use of polymer material are:

- Autooxidation: thermooxidative (T, O₂) and photooxidative ageing (h_v, T, O₂)
- Resistance to chemical attacks and possibly to additional simultaneous mechanical stress (σ) (environmental stress cracking behaviour, ESC)
- Biodegradation

Durable static or dynamic stress leads to a technical break down of a material. Figure 2 summarizes relevant effects. It has to be mentioned, that mainly chemical modifications influence the visible and physical changes.

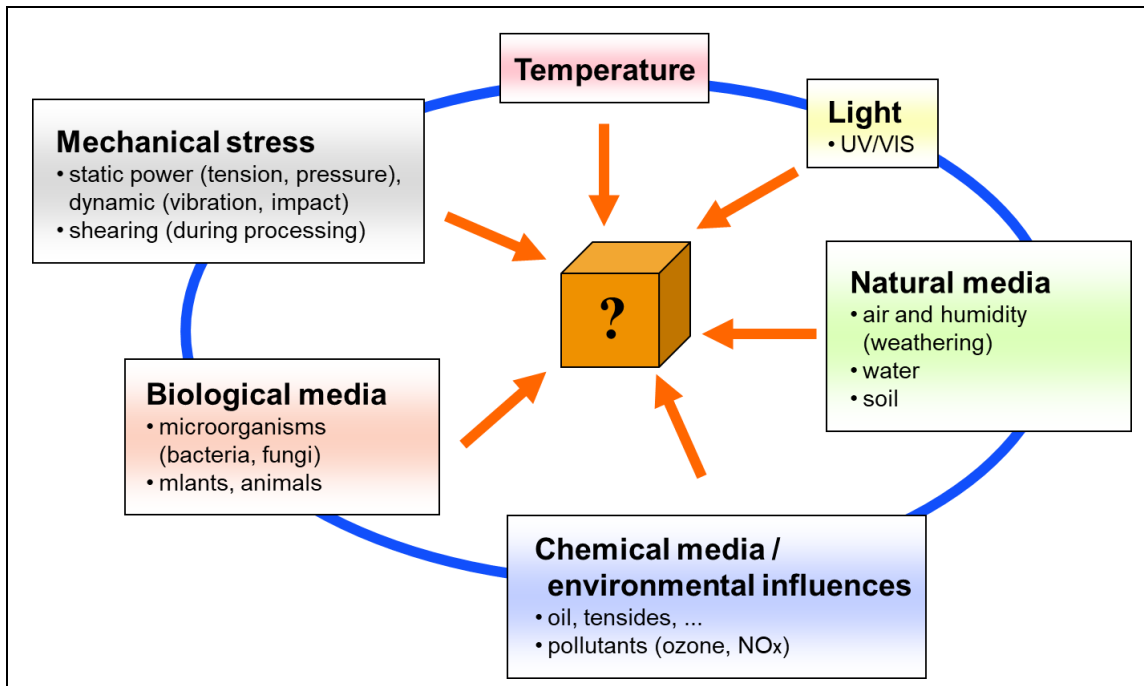


Figure 1: Stress influences on polymers

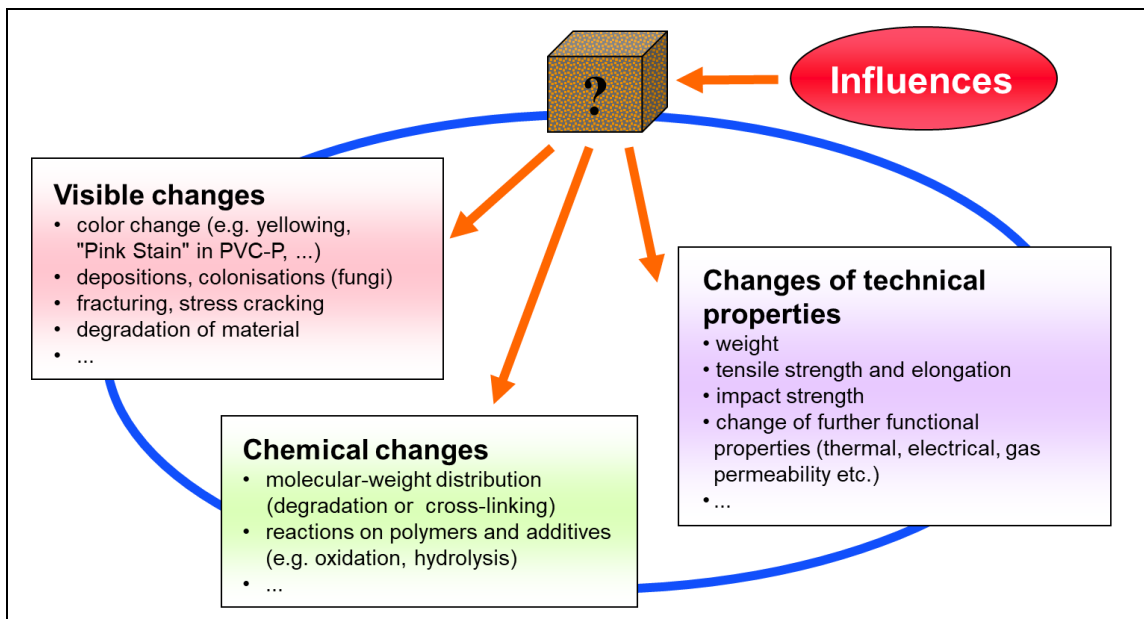


Figure 2: Effect of stress influences on polymers

2. Autooxidation

The term autooxidation [1,2,3] corresponds to the autocatalytical oxidation of polymers. The relevant reactions and the cycle of the autooxidation are stated on figure 3. The initiation of autooxidation contains the following important reaction steps:

1. The reaction starts by generating radicals $R\bullet$ (molecules with an unpaired electron) due to different stresses:
 - shear (τ) during processing / moulding
 - heat, thermal energy (T)
 - high energy light radiation ($h\nu$)
 - influence of (redox-active) metal ions M^{n+} , e.g. catalyst residues (titanium, chromium, aluminium, iron) or extrinsic metal ions (iron, copper, e.g. in electro-cables)
 Hydrocarbonaceous polymer chains form aliphatic radicals (C-atom contains an unpaired electron).
2. Oxygen in its diradical triplet-shape $|\overset{\cdot}{O}-\overset{\cdot}{O}| \equiv |O=O|$ immediately reacts with generated alkyl radicals (practically without activating energy) to the peroxy radical $ROO\bullet$.
3. The reaction of the peroxy radical with RH to hydroperoxide $ROOH$ is rate determining.
4. After the generation of $ROOH$ to the autocatalytic chain reaction keeps going on. In addition redox-active metal ions M^{n+} catalyse the decomposition of hydroperoxyde.

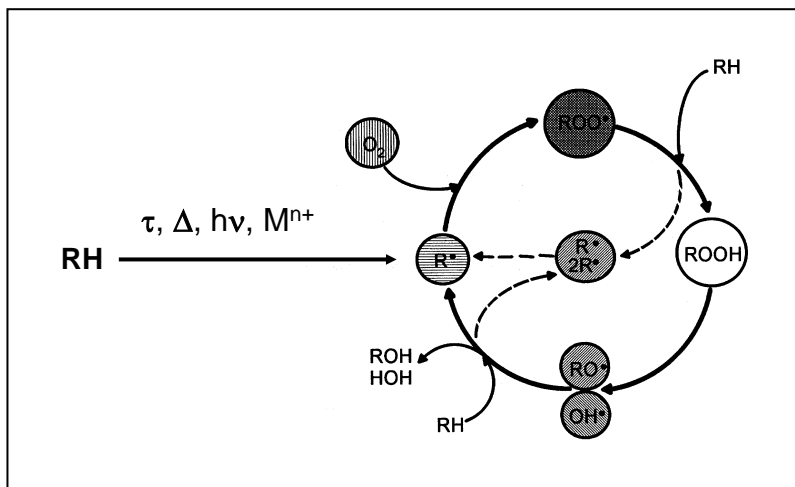


Figure 3: Cycle of autooxidation [3]

The rate-determining step for the formation of hydroperoxyde during the autooxidation reaction retards the following chain reaction (induction period). After this induction period quick changes of different properties can be observed. Figure 4 presents schematically changes of relevant properties:

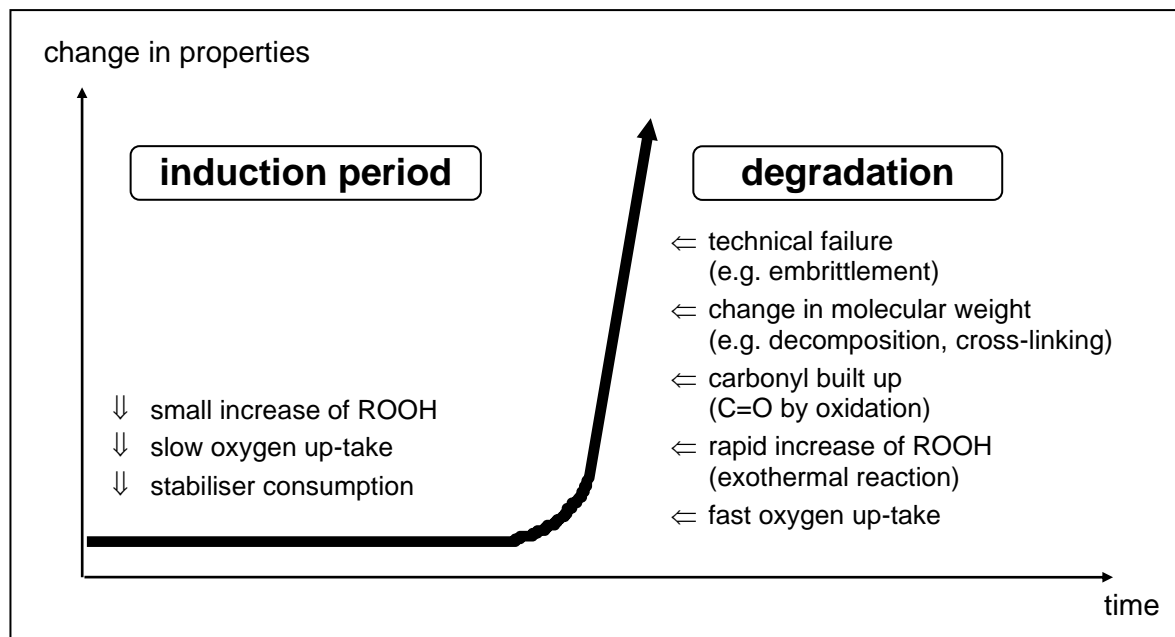


Figure 4: Change of properties after the induction period. [3]

Overall, the autooxidation is a reaction between a gas (oxygen) and a solid phase (polymer). Diffusion and solubility of O_2 are material depending and influence the oxidation reaction significantly:

- At ambient temperature polymer materials are normally oxygen saturated, which lead to a homogeneous and thickness independent ageing of the material. (see figure 5).
- Thermal processing or strongly accelerated heat-ageing (high T) of thick samples can lead during the induction period to a local lack of O_2 due to a high consumption of O_2 and a too slow diffusion rate determined supply of O_2 . Therefore the started chain reaction is locally less oxidative (e.g. in the inner part of an element, see figure 5).
- The diffusion of oxygen depends on the ability to produce free volume in the material. The more flexible the polymer chains segments are (i.e. the bigger the difference $T_{use} - T_g$), the higher the diffusion rate.
- Oxygen is soluble only in amorphous areas. Crystalline areas are significantly more inert against autooxidation

A characteristic feature of the autooxidation as ageing process is, that chemically and physically released changes of the material are in general not reversible.

2.1. Thermooxidative ageing

The term „thermooxidative ageing“ means the influence on materials by heat energy in presence of oxygen. From scientific point of view the involved processes (autooxidation) and changes are widely understood due to the small number of influencing parameters (temperature, oxygen partial pressure) [1,2,3].

Table 2 gives an overview on the most important and easily recognisable effects on thermoplastic materials by heat treatment. The result is, that polymers with different structures show different behaviours.

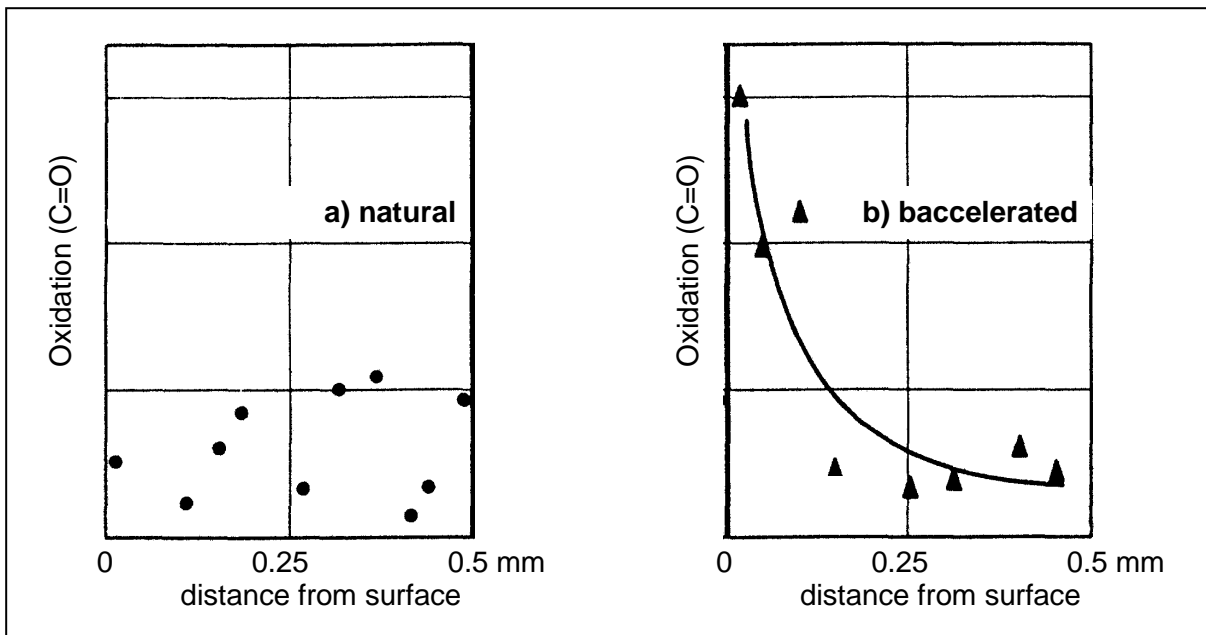


Figure 5: Extent of the oxidation (C=O carbonyl built-up) of PE-foils (thickness 1 mm) at natural (room temperature) and accelerated thermal ageing ($T = 90^{\circ}\text{C}$) in dependence from the distance of the surface [4]

Table 2: Effect of the thermooxidative ageing on thermoplastic materials [1]

Criteria	PE, PP	PS	PMMA	PVC	POM	PA	PET	PC
• embrittlement	XX					X		
• yellowing	X	XX	X	XX	X	X		XX
• tensile strength • and elongation	X	X	X	X	X	XX	XX	
• impact strength	X	XX	XX	X	X	X	X	X
• bending strength	X	X						
• intrinsic viscosity						X		X
• loss in weight					XX			

XX = main criterion, X = auxiliary criterion

For the accelerated simulation of the thermooxidative ageing processes the following laboratory tests are frequently applied using higher temperature and/or the oxygen partial pressure:

- Accelerated oven ageing, mostly at a temperature below the melting temperature, resp. flow temperature, with subsequent characterization of the relevant properties (e.g. according to table 2)
- Determination of the oxidation-induction-time by differential scanning calorimetry (DSC, e.g. according to ISO 13357-6 or chemiluminescence).

Due to acceleration, the reaction processes are getting possibly modified (kinetics, reaction products); whereby a relevantly aspired extrapolation of the service live determination of a component is getting complicated (see chapter 5).

2.2. Photooxidative ageing

The term „photooxidative ageing“ means the influence on materials by light energy (photons, $h\nu$). It plays a major role particularly on outdoor application of materials. Besides light energy, there are also other parameters, which can influence the ageing processes:

- radiation source: radiation intensity (maximum intensity of irradiation, e.g. in Europe, ca. $1000\text{W}/\text{m}^2$); radiation spectrum (wavelength range λ of the global radiation from 300 to $>1500\text{nm}$); radiation cycle (e.g. day - night).
Generally the most sensible are polymer materials in the range of UV-A (400-320nm) and UV-B (320-280nm).
- environmental temperature (-30 to $+50^\circ\text{C}$)
- air humidity / wetting (drop as lens!)
- partial pressure of oxygen
- industrial pollutants (pollutant gases: SO_2 , NO_x , HCl , O_3 , acid precipitations: H_2SO_4 , HNO_3 , HCl ; aerosols and chemically loaded soot particles)
- material specific influences: light absorption (especially in the range of UV, but also inherent colours); degradation sensitivity depending on the wave length λ ; temperature of the sample (influenced by radiation extents, inherent colours and ambient temperature, sample temperature up to 100°C possible)

Outdoor weathering tests are due to their realistic ratings, despite of the long run exposition periods essential. In practice, the samples of interest are placed in exposure sites, which are south oriented in the northern hemisphere. The test samples are positioned in an angle of 45° to the earth's surface. Weather stations are an advantage because all relevant weather influences (radiation, temperature, humidity, and pollution) are registered. Due to the locally different environmental conditions the measured values are, strictly speaking, only valuable for the respective weathering test place.

For the simulation and acceleration of the photooxidative ageing test devices are used, where the influence parameters radiation (intensity, energy distribution), heat, humidity and rain, possibly pollutants can be chosen and/or regulated in a broad range. The kinetics and the effect of the initiated degradation reaction by photons depend however on the choice of the radiation source, which must be carefully selected. The following sources are common: xenon arc lamps, UV-lamps and carbon arc lamps; details see [1,5] and ISO 4892-1 to -4.

Artificial weathering tests have the advantage of shorter test periods and the independence of locations, seasons, local climates, air-pollution etc. Those test results give a direction on the weathering resistance of a polymer compound under reproducible conditions to the application engineer.

In general, the experience shows, that between the results of the artificial weathering and the outdoor weathering a rank correlation is detected if appropriate test conditions according to relevant standards are used. To receive relevant test results, the weathering devices should accomplish the following conditions:

- The wavelength range and the intensity of the degrading radiation has to correspond with the local solar radiation (UV and visible range).
- The humidity on the sample surface corresponds with the one of the natural weathering.
- Day and night-cycles (darkroom storage) can be simulated.

Table 3 gives an overview on the most important and easily recognizable effects induced by photooxidative ageing. These effects partially differ significantly from the observed changes caused by the thermooxidative ageing (see table 2). This difference can be explained by the more complexive stress conditions and by partially deviating chemical reactions (e.g. light-induced hydroperoxide degradation, hydrolysis, etc.).

Table 3: Effects of the photooxidative ageing on thermoplastic materials [1]

Criteria	PE, PP	PS	PMMA	PVC	POM	PA	PET	PC
• yellowing	X	XX	XX	XX		X		XX
• surface cracks chalking	X	X			XX			
• tensile strength & elongation	XX		X	X		XX	XX	
• impact strength	X	X	XX	X	XX	X	X	X
• bending strength		X			X		X	

XX = main criterion, X = auxiliary criterion

2.3. Stabilisation

Suitable antioxidative agents (stabilisers) [1,2,3] protect polymers against the degradation by air oxygen (O_2), heat (T), solar light ($h\nu$), shearing (τ), metal ions (M^{n+}). They cause a retardation of the ageing process (see figure 6). Thus the life time of the material can be extended essentially.

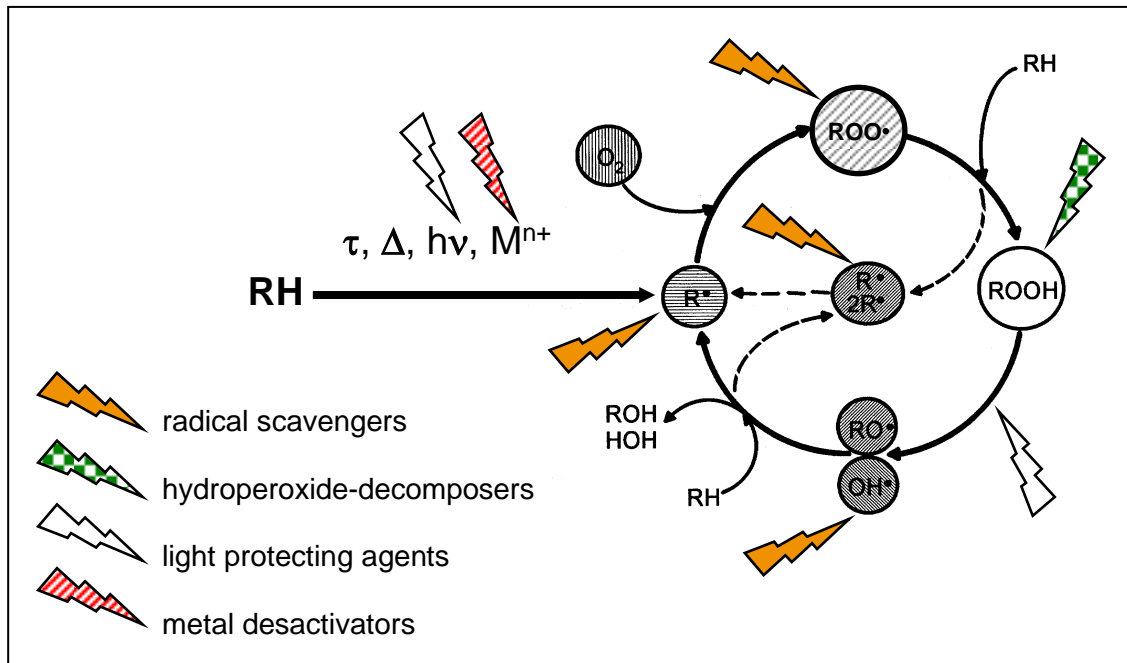


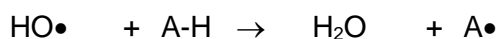
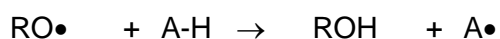
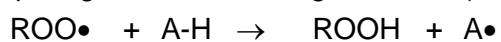
Figure 6: Stabilisation possibilities

Four types of stabilisers are differentiated, which are normally added in an amount of 0.01 to 2% relative to the polymer:

- **Antioxidants / radical scavengers (primary antioxidants):**

They protect against degrading influences of oxygen and heat during the production, moulding and the service life. In general, the hydrogen-donors and radical absorbers lead to an interruption of the chain reactions during the autooxidation process. The stabilisers get used irreversibly in dependence on the stress.

Participating chain terminating reactions (AH = antioxidants with H-donor):



Examples:

- sterically hindered phenols (main reactivity with peroxy radicals)
- sterically hindered aromatic amines (main reactivity with peroxy radicals)
- sterically hindered amines (also HAS = hindered amine stabiliser; main reactivity with peroxy-radicals; probability to form nitroxyl-radical Alkyl-N-O•)
- benzofuranone-derivates (main reactivity with alkyl radicals)

- **Costabilisers / hydroperoxyde decomposers (secondary antioxidants):**

The efficacy of the primary antioxidants are significantly improved by these additives (synergistic effect, see figure 7). Arising hydroperoxides are reduced to alcohol and therefore withdrawn to the autooxidation process. The stabilisers are consumed/oxidized irreversibly due to the variation with stress.

Examples:

- phosphorous acid esters (efficacy during moulding process)
- thioether (efficacy during long term application)

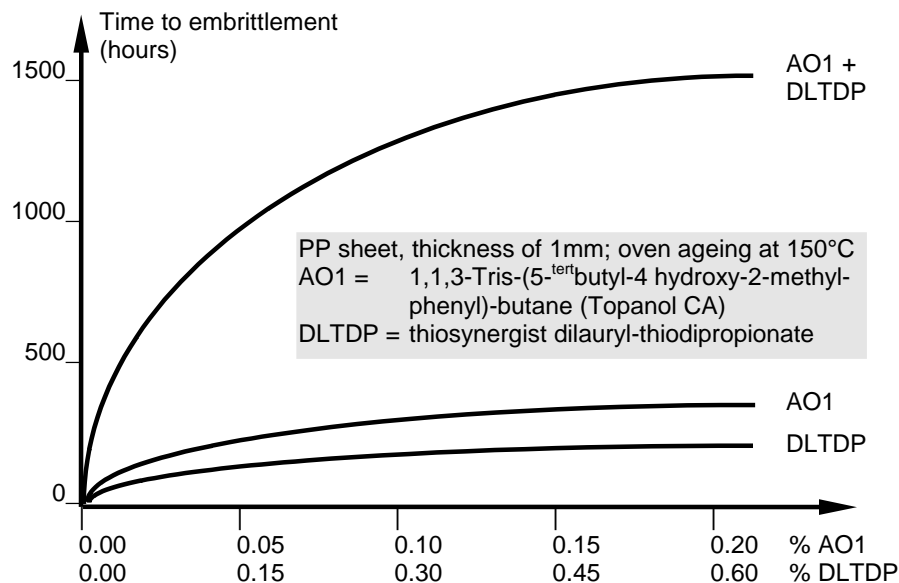


Figure 7: Example of the synergistic effect of a costabilisator

- **Light protecting agents:**

They increase the light-resistance; an outdoor application of polymers becomes possible. Two types of light protecting agents are used:

- **UV-absorbers** absorb the deleterious UV-radiation (Lambert-Beer law) and transform light-energy to heat. Their efficacy increases with increasing distance from the component surface and reaches normally a maximum of about 100 μm .
Examples: hydroxybenzophenones, hydroxybenzotriazoles, cinnamic esters and oxalanilides.
- **Quenchers** withdraw by light energy activated molecular quota; they operate independent of the coating thickness and are therefore qualified for fibres and thin foils: Examples: metalorganic nickel compounds; not market relevant.

Both types cannot be destroyed by action of light. Their function remains therefore active during the whole lifetime (except for material specific losses by migration and evaporation).

For an increased protection against photooxidative ageing additional radical scavengers respectively hydroperoxide decomposers are used. Sterically hindered amines (HAS) proved to be very reliable and showed a behaviour similar to the mentioned quenchers.

- **Metal deactivators:**

The deleterious influence of redoxactive transition element (e.g. system Cu^+ , Cu^{2+}) are reduced or totally annulled with appropriate chelate ligands.

The following relevant properties beside the protecting functions are required for these additives: e.g. a high compatibility with the polymer, low losses due to production and service life, long time stability, etc. Therefore it is not astonishing, that a broad range of different additives is available to satisfy the different requirements.

Apart from the antioxidative agents often further series of additives are added to the polymer material, which can partly influence the autooxidation positively or negatively.

Examples:

- Carbon black as a filling agent or pigment acts in addition as a light absorber, which transforms light energy into heat energy.
- Titanium dioxide (TiO_2) as white pigment exists in two different crystal modifications: anatase and rutile. As pigment practically only rutile is used because anatase has significantly stronger oxidizing properties.

Figure 8 summarizes the relevant parameters, which have to be taken into consideration for the development of stabilising formulations for functional components.

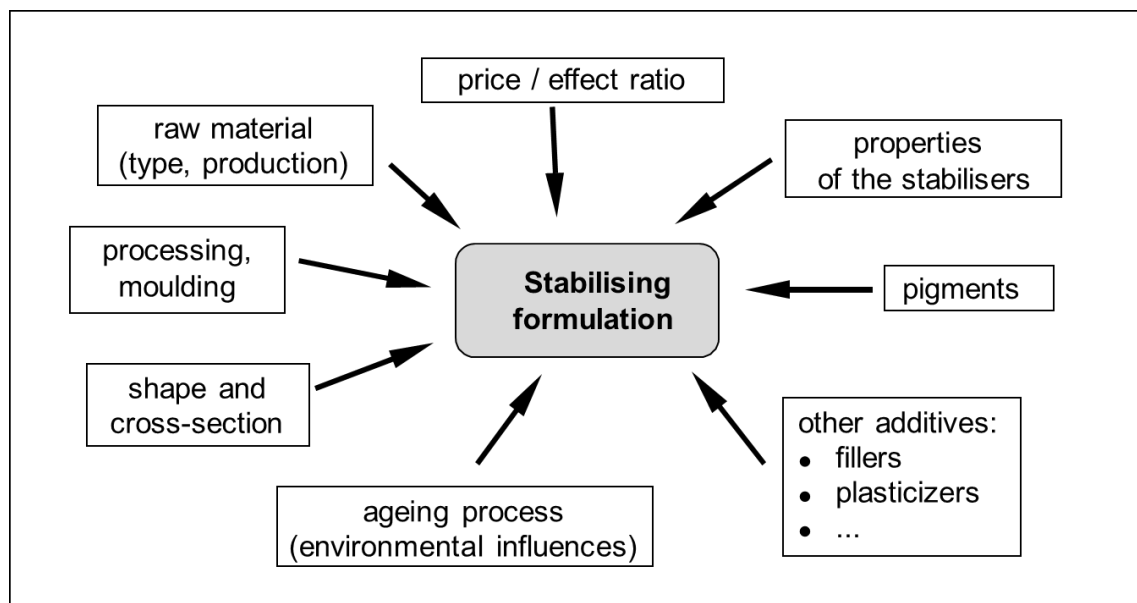


Figure 8: Influencing factors on the stabilising formulation

3. Chemical Resistance

Many plastic products get in contact with different media during their service life:

- mineral oils, e.g. hydraulic oils, motor oils, gearing oils etc.
- silicon oils (lubricating agent and antiblocking agent)
- lubricating greases
- vegetable and animal oils and grease
- break fluid on a glycol base
- motor fuel, diesel etc.
- organic solvents, e.g. alcohol, ethers, esters, etc.
- water and aqueous solutions of acids, alkalines, tensides, etc.
- organic and inorganic acids (oxidant and non oxidant)
- refrigerating agents, e.g. ammonia, freon etc.
- gases and vapours

The durability of polymer materials [2,6,7] is usually specified in tables by means of the following qualitative terms

resistant --- moderate resistant --- not resistant

Evaluating a material these informations are necessary for the user. For a selective material development with a defined list of requirements indeed further quantitative gaugeable criterions must be taken into account for the estimation of changes after stress influence.

The influence of chemicals on a material has different effects; two different types of processes can be distinguished:

- Physically influencing media do not react with the plastic material. But they lead to swelling (increasing of elasticity, decreasing of hardness and T_g) up to dissolution and with it to reversible changes of the properties of plastic materials.
- Chemically influencing media react with the plastic and modify its properties irreversibly. It is characteristic for the degradation of plastic materials, that even small chemical transformations can cause distinct changes of the physical properties.

A further phenomenon to be mentioned is the topic **Environmental Stress Cracking (ESC)** [6,7,8]: At coincident interaction of a medium and a mechanical tension (or also after moulding built up frozen tension) on a polymer material, cracks can arise which penetrate slowly from the surface into the interior and lead finally to material ruptures. This effect represents a serious impairment of the functional properties, because of a sudden and often unexpectedly a polymer component can fail, even after a long-term troubleproof application.

ESC properties of materials are characterized e.g. by application of pulling or bending forces on immersed material samples, whereas the elongation versus time are recorded. These creep tests (see figure 9) are usually of long duration. In a newer development project, the tension is linearly increased with the time, by what within shorter period ESC properties (polymer-medium) can be determined [9].

The behaviour of thermoplastics in respect to chemicals is very different and depends on various factors. Table 4 informs about the material specific behaviour of individual thermoplastics.

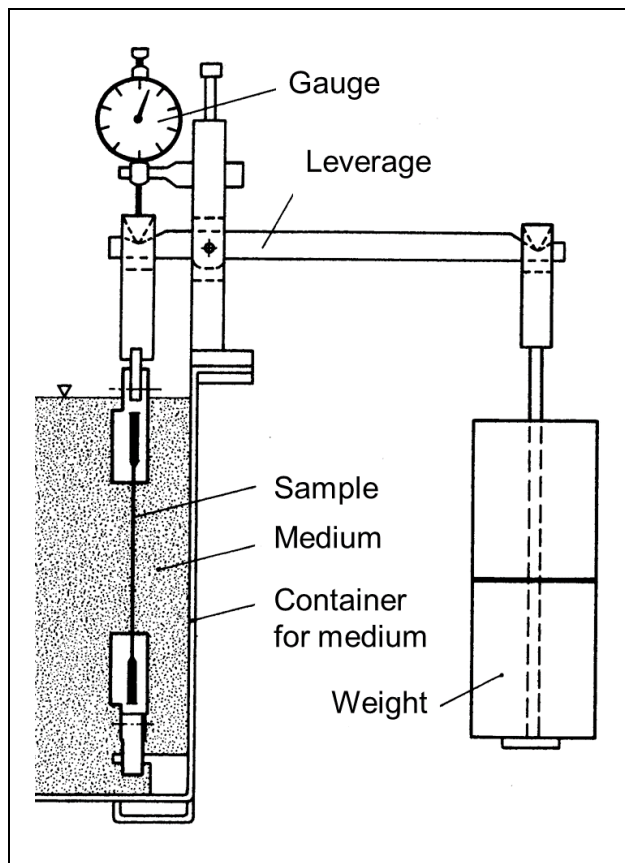


Figure 9: Long-time creep tests in contact with chemicals

Table 4: Chemical resistance and tension crack sensivity of thermoplastic materials

Material	A	L	OX	AL	K	E	CI	AR	HC	ESC
PE-LD	+	+	-	+	+W	0W	-W	-WS*	0	yes***
PE-HD	+	+	-	+	0	0	-W	-WS*	0	yes***
PP	+	+	-	+	0	0	-W	-WS*	0	yes***
PS	0	+	-	+E	-S	-S	-S	-S	0	yes
PMMA	0	0	-	0E	-S	-S	-S	-S	+	yes
PVC-U	+	+	0	+E	-W	-W	-W	W	+	low
PVC-P	0	0	-	-W**	-W**	-W**	-W**	-W**	-W**	low
POM	-	0	-	+	+	0	0	+	+	low
PA 6,6	-	0	-	0	+	+	+	+	+	low
PET	0	-	-	+	-	0W	+W	0	+	no
PC	-	-	-	+E	-W	-W	-S	-W	+	yes
CA	-	-	-	0	-W	-W	0W	W	+	low

Used abbreviations:

- Chemicals: **A** = mineral acids (HCl), **L** = alkaline solutions (NaOH), **OX** = strongly oxidising agent, **AL** = alcohol, **K** = ketone (acetone, methyl-ethyl-ketone), **E** = ester (acetic acid ethyl ester), **CL** = halogenated hydrocarbon (chloroform), **HC** = aliphatic hydrocarbon (hexane), **AR** = aromatic hydrocarbon (toluene);
- Resistance: **+** = resistant, **0** = moderately resistant, **-** = not resistant, **E** (or **ESC**) = ESC susceptible, **S** = soluble, **W** = swelling
- * = at high temperature, ** = plasticizer leachable, *** = specific surface-active tensides of detergents

3.1. Mechanisms

The relevant mechanisms are the interaction of the polymer material with the medium, which could lead to swelling / dissolving of the polymer, and the transportability of the medium by the polymer (diffusion).

- **Swelling or dissolving:** The swelling or dissolving tendency of polymers can roughly be estimated by the polarity differences between the contact partners polymer and medium.
- **Diffusion:** The deterioration of the functional properties of thermoplastic materials by the interaction with physical or chemical active media is very closely connected with the amount of the agent diffused in the polymer. If it cannot penetrate into the polymer, the two components can only get in contact with the surface of the polymer. In case of an active medium the reaction with the polymer, remains on the surface and the materials properties are not significantly influenced. In most cases the medium diffuses more or less quickly in the material, therefore the diffusion rate is the main factor, which determines the rate of the decomposition of polymer materials due to effects of an aggressive agent (see figure 10).

The transport of a low molecular substance through a polymer bases mainly on an activated diffusion, which depends on the polymer structure (interaction between polymer chains), the temperature (exceeding of the activating energy), on the molecular weight and shape of the diffusing substance and on the interaction between the substance and the polymer. The central process is the generation of locally displacing "free volume" by thermal movement of the polymer chain segments. However, submicroscopic capillaries, which exist as micropores in polymers, can also transport substances.

The transport processes of low molecular substances through a polymer matrix are temperature dependent. At increasing temperature, the rate of diffusion is rising. The increase below the glass transition T_g is significantly smaller than above it. (see figure 11).

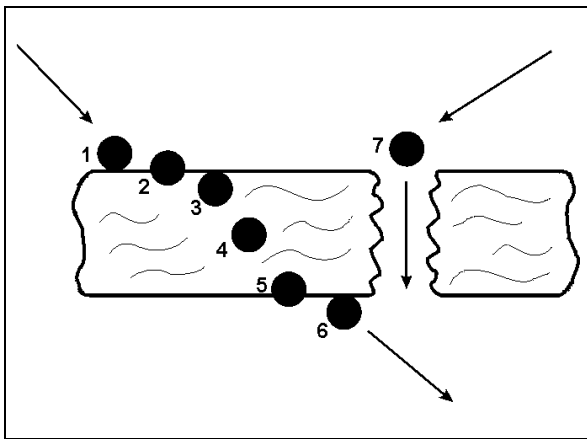


Figure 10: Diffusion process [1]:
1. adsorption, 2. absorption, 3. dissolution,
4. diffusion, 5. desorption, 6. evaporation,
7. direct transmission (through micropores)

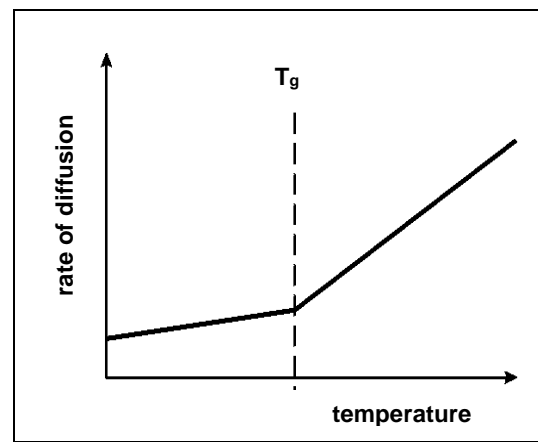


Figure 11: Temperature dependent rate of diffusion

3.2. Hydrolysis

The hydrolytic degradative reactions are involved in several processes:

- moulding and processing (reactivity of residual in polymers at high temperatures)
- weathering (acid-catalyzed hydrolysis of residues of non volatile H_2SO_4)
- biodegradation

The hydrolytic degradation of thermoplastics is promoted by two factors:

- Thermoplastics have the capacity to absorb greater quantities of water depending on polarity and affinity to water.
- Hydrolytic reactions are normally catalyzed in the presence of acids and alkalines due to the high polarity of the attacked groups.

The following functional groups in the material are susceptible to hydrolysis in particular: esters, amides, carbonates, urethanes, nitriles, ethers etc. The effect of the hydrolytic reaction is different: If the main polymer chain is cleaved, stronger changes of properties have to be expected as if functional groups beside the polymer chain get hydrolysed (e.g. polyacrylonitrile, polyvinyl acetate).

Table 5 summarizes the subject to hydrolysis polymers.

Table 5: Properties of thermoplastics susceptible to hydrolysis [6,7]

Polymer	Water-absorbing capacity at 23°C		Hydrolysis catalysed by
	in water	in air (50% rF)	
PET	1-2	0.1	slightly by acids and alkalines; *,**
PA 6	10	3	by acids; **
PA 12	1.5	0.5	by acids; **
PC	0.4	<0.1	by alkalines
PU	0.5-5	-	by acids
POM	1	-	by acids; ***

*) less susceptible to hydrolysis at application temperature due to aromatic structure

***) strong susceptible to hydrolysis during processing (predry necessary!)

****) the autooxidative degradation can form formic acid, which catalyses the hydrolysis

3.3. Stabilisation

With regard to the protection of polymer material against chemicals, the developed procedures are not yet so far advanced like e.g. the stabilisation against the thermooxidative, the photooxidative or the biological degradation. In this area there is no systematic research. One of the main causes of the actual status is the fact, that an increase of the durability of plastics against the influence of an aggressive medium often requires wide interventions in the composition and the structure of the polymers. In fact, the effort is comparable with the effort for the development of a new polymer material.

A certain increase of the swelling resistance in physically active media can be achieved by cross-linking, increase of the crystallinity, by orientation of the molecules or by surface modification.

Additives like plasticisers and fillers can also modify the behaviour of a plastic to a certain extent.

As protecting agents against hydrolysis under service conditions (ambient temperature, moderate air-humidity) often sterically hindered, slowly by water abreacting carbodimides are used. As acid-acceptors metal carboxylates are utilized.

4 Biodegradation

The requirements for a biological ageing of polymer materials are [2,7,10]:

Organisms:

- macroorganisms: rodents, insects, worms, plants (roots)
- microorganisms: algae, bacteria, fungi

Nutrition substrates:

Fundamental conditions:

- breakable chemical bonds: esters >> urethanes = amides > ethers
- low molecular weight (more preferred than high Mw)
- soft material (in general easier degradable than solid material)
- hydrophilic polymers (in general better degradable than hydrophobic)

Typical chemicals:

- aliphatic hydrocarbons with Mw < 1000 (lubricating agents, partly degraded polyolefines)
- some aliphatic esters e.g.:
 - adipate and sebacate as plasticisers in PVC
 - polyesterurethanes
- as biodegradable indicated, ester containing polymers (polycaprolactame (PCL), poly (3-hydroxybutyrate) (PHB), poly (3-hydroxyvalerate) (PHV), polylactides)
- some ether groups in polymers e.g. with a polysaccharide structure
- aliphatic alcohols, e.g. polyvinyl alcohol

Commodity plastics are in general „bad“ biodegradable substrates

Suitable environmental conditions:

- humidity (63-99% rF), pH (4.5-8.5), salinity (e.g. nitrate as nitrogen source)
- fertile temperature (10-40°C)
- oxygen concentration:
 - aerobic conditions (with O₂): a mineralisation of organic carbon to CO₂ is possible
 - anaerobic conditions (without O₂): the degradation of organic material leads for example to methane gas
- presence of cosubstrates

4.1. Processes

Biological ageing is not always destroying polymer materials. If the materials are colonised by organisms, the following effects are possible:

1. The material is inert and doesn't sustain modifications.
2. By colonisation with microorganisms the material can change the colour (e.g. yellowing), but there are still no changes of important functional properties observed.
3. The properties of the material change by microbial colonisation: fungi, lichens or roots are releasing substances, which can attack the material.
4. Rodents gnaw a material, even if the material is no substrate.
5. A material is a substrate, gets degraded and digested.

The biologic degradation of polymers is characterized by the following properties:

- Decomposition of the three-dimensional structure
- Reduction of the mol masses by exoenzymes
- Absorption of fragments and degradation in the cells of the organisms

Biochemical and biophysical processes are differentiated, as shown below:

Biochemical processes: microorganisms and bigger creatures are releasing metabolites. These react, once excreted, like chemical substances. The effect on plastics corresponds therefore to the chemical resistance of the material against these chemicals. Microorganisms produce the following chemicals:

- Acids are often released substances. Depending on the involved organisms and their metabolism organic acids (by chemo-organotropic organisms, e.g. oxalic acid) as well as strong mineral acids (by chemo-lithotropic organisms, e.g. nitric- and sulfuric acids) can be formed.
- Enzymes are special proteins, which can catalyse chemical reactions. Enzymes, which are able to attack esters groups, are called esterases. Other enzymes selectively catalyse the cleavage of polymers, splitting off monomers or oligomers. Microorganisms often are only producing certain enzymes if the corresponding substrate is available. Many polymer materials get especially then attacked when different organisms and/or enzymes “cooperate” simultaneously.
- Many microorganisms produce colouring substances. Some of them are water-soluble, others penetrate e.g. PVC-P and produce non removable pigment spots like „Pink Stain“. In general, colouring substances do not destroy the material, but effect on certain ranges of application a high reduction.

Apart of the metabolic products the environmental gas atmosphere plays an important role influencing the microbial metabolism. The degradation of these materials under aerobic conditions (with O₂) by aerobic living microorganisms leads to a complete mineralisation to water and carbon dioxide, under anaerobic conditions polymers degrade also to methane and other not completely oxidised products.

Biophysical processes: The penetration of plant roots and the reduction to smaller pieces by rodent gnaw are examples of physical processes. These processes are often connected with chemical processes: acid segregation at the roots points prepares the penetration; materials gnawed by rodents are often reduced to smaller pieces and degraded by metabolites.

4.2. Stabilisation

Biological ageing of some polymers is not desired. In such occasions appropriate biostabilisers with a broad range of antimicrobial activities are added [2]. In using biostabilisers the microbial colonisation is suppressed. Since bacteria, fungi and other microorganisms live in the water phase, the biostabilisers should be sparsely soluble in water. Therefore, after a long-time exposition period the protective effect will exhaust.

Further requirements on biostabiliser are e.g:

- compatibility with the polymer and other additives
- processibility at high temperatures
- no negative influence on other ageing processes (heat, weathering)
- low toxicity for warm blooded animals

A large number of materials are proposed as biostabiliser; but only a few of them succeeded on the market. Most of them contain heavy metals (arsine, antimony copper, tin). There also exist root adverse additives or animal repellents, e.g. on the base of hormones and odours.

While some materials should be resistant against biodegradation, other polymers should be completely biodegradable. The latter polymers [10] are characterized by the following properties:

- They were completely mineralised (the carbon of organic components is completely transformed to CO₂)
- Neither the metabolites nor the non degradable components should have a toxic effect.

5. Extrapolation of the Lifetime by Accelerated Ageing Tests

It often is a target to achieve by means of accelerated ageing tests by increase of individual parameters (e.g. temperature, O₂ partial pressure, light intensity, concentration of pollutants and chemicals) statements concerning the lifetime of a component. An approach according to Arrhenius is applied mostly:

$$\log t_e = a + b \cdot \left(\frac{1}{T} \right)$$

whereas: t_e = time up to the appearance of a defined property change in the material

- e.g. half-time up to 50% reduction of a property (tensile strength and elongation, ...)
- e.g. embrittlement time by oven ageing or oxidation induction time by DSC at a given temperature

T = absolute temperature in Kelvin

a = axis intercept

b = slope of the line

Figure 12 shows a typical Arrhenius-plot. Contrary to the expectation no fully linear correlation can be observed; therefore, a reliable extrapolation of the life time at ambient temperature is hardly possible. That indicates that an approach according to Arrhenius can lead to distorted lifetime prediction. The following factors influence the trend of an Arrhenius plot significantly:

- Different reaction rates of the involved reactions (autooxidation, decomposition by chemical attacks) in dependency of the temperature (varying activating energies).
- Phase transitions of polymers (e.g. glass transition, melting, formation of more free volume, ...) and maybe also of additives.
- Component size: starting at about 100 μm the thickness of a component leads to a locally different oxidation behaviour and with it also to a deviating mechanical break down; see figure 5.

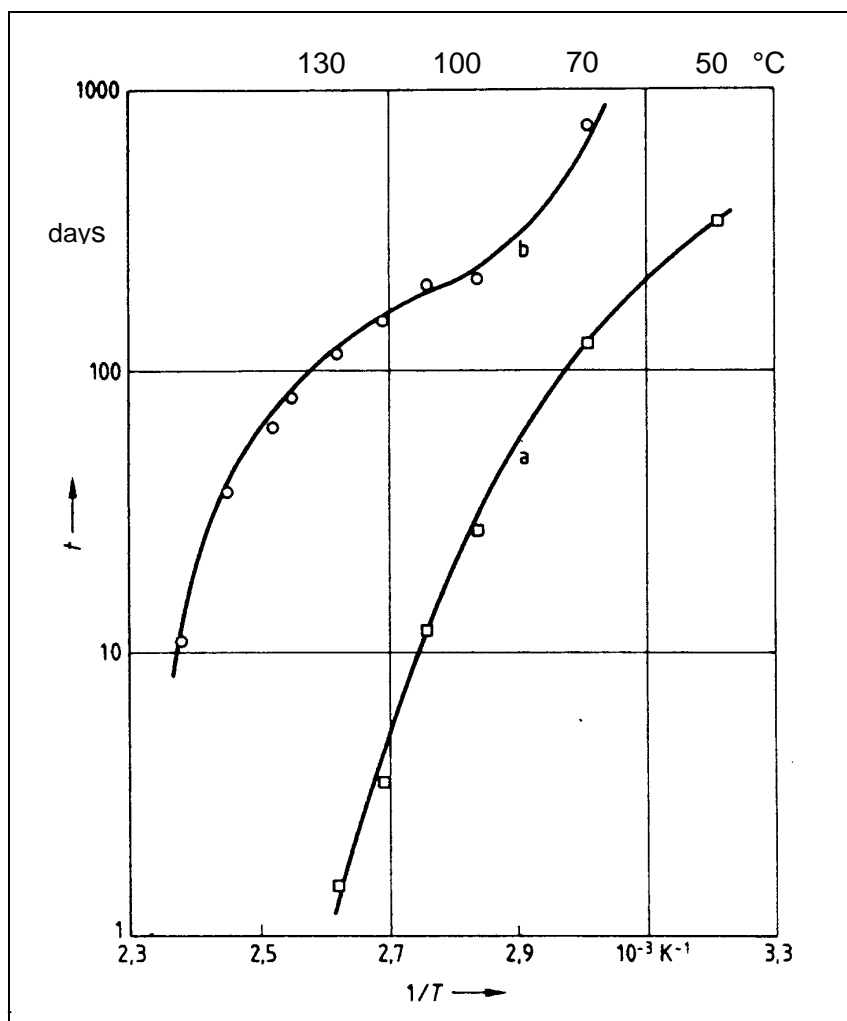


Figure 12: Arrhenius plot $1/T$ vs. embrittlement time t of a 120 μm thick PP foil; a) without antioxidants, b) with 0.05% Irganox 1010; [2]

A lot of literature citations proof, that accelerated ageing tests with polymer material in general, not necessarily lead to a reliable prediction of a realistic service life of components and therefore have merely an orientating character. The prime reason remains - as mentioned before - in the complexity of stresses during service and thereby initiated reaction- and reactivity diversity. Reliable extrapolations are only successful if accelerated tests are preferably configured as field-experienced as possible, however mostly at the expense of time gained.

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