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Sample Pages

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Resistance and Stability of Polymers

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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].

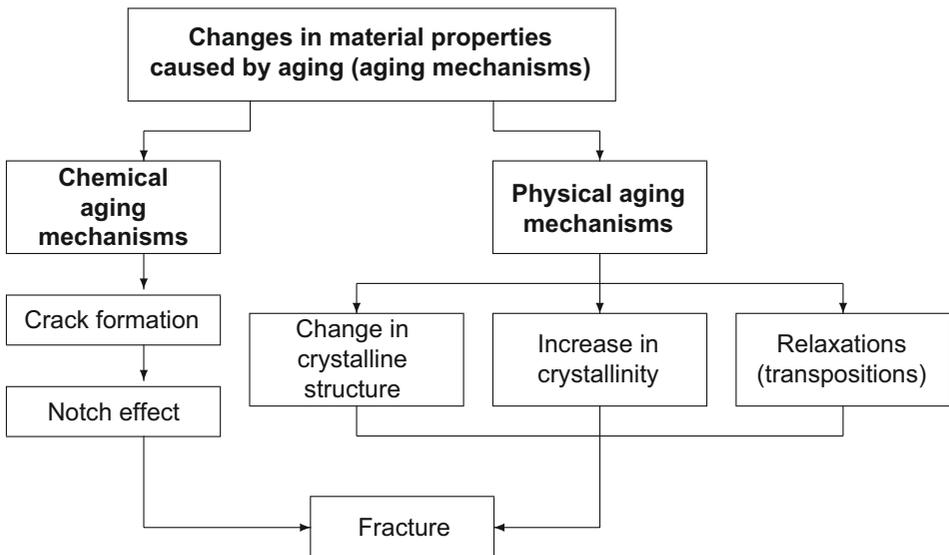


Figure 1.4 Simplified diagram of aging processes [18]

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].

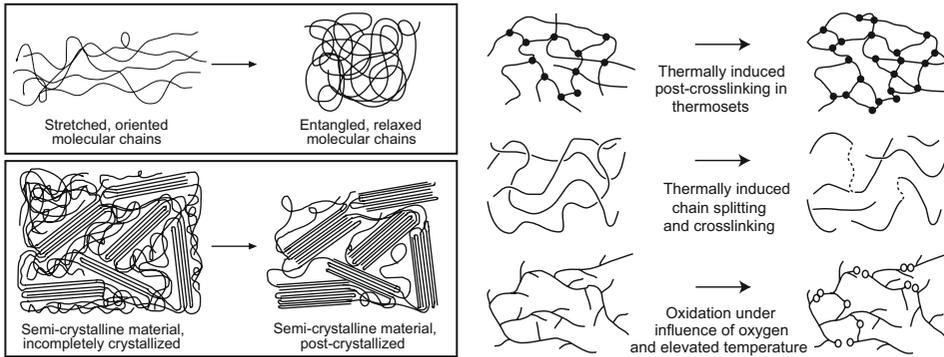


Figure 1.5 Effects of aging [19]

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].

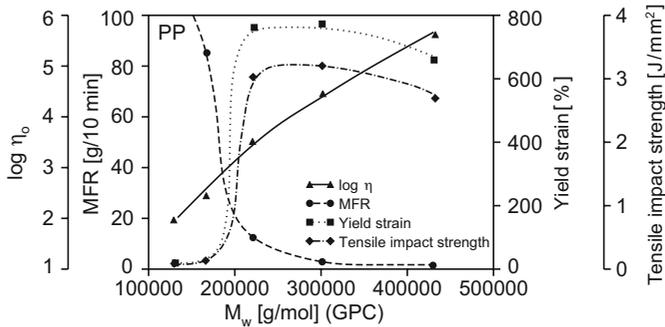


Figure 1.6 Mechanical and rheological properties of a polypropylene homopolymer as a function of molecular weight (at comparable index of dispersion) [21]

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].

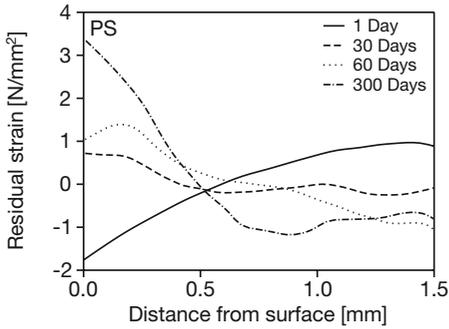


Figure 1.7
Residual stress distribution (detected by removal of layers) in flat shoulder test bars made from polystyrene ($T_m = 200\text{ }^\circ\text{C}$, $T_w = 30\text{ }^\circ\text{C}$) after different aging periods at $23\text{ }^\circ\text{C}$ [24]

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].

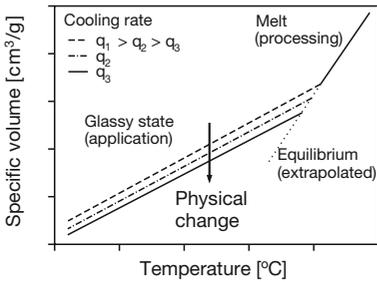


Figure 1.8
Schematic illustration of the dependence of specific volume on temperature [28]

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

■ A.13 Fluoropolymers

A.13.1 Chemical Resistance of Fluoropolymers

Table A.34: Chemical resistance of fluoropolymers; S = swelling; temperature is provided in [32], temperature is not provided in [1039]

| | |
|-----|-------------------------------|
| A = | Excellent chemical resistance |
| B = | Limited chemical resistance |
| C = | Not chemical resistant |

| Medium | Resistance | | | | Comment |
|----------------------------|------------|------|---------------|---------------|---|
| | PTFE | ETFE | PVDF | PCTFE | |
| Abietic acid | | | | 20 A | |
| Acetamide, 50% | A | A | A | | |
| Acetate (Na, K and others) | | | 100 A | 100 A | |
| Acetic acid, conc. | A | B | 50 A 100 C | 20 A 80 C | |
| Acetic acid, 50% | | | 100 A | 80 A | |
| Acetic acid, aqueous, 10% | A | | A | | |
| Acetic acid, aqueous, 5% | A | | A | | |
| Acetic anhydride | | | 20 B | 60 A 120 B | PCTFE: acid uptake 3.1% |
| Acetone | A | A | 20 C 20 C | 20 A 60 B | PVDF: partial dissolution; PCTFE: S = 2.8% |
| Acetonitrile | | | 50 A | | |
| Acetophenone | | | 20 A 50 C | 50 A | |
| Acetyl chloride | | | 50 A | | |
| Acetylsalicylic acid | | | 50 A | 50 A | |
| Acrylonitrile | | | 20 A | | |
| Adipinic acid | | | | 50 A | |
| Allyl alcohol | | | | 20 A | |
| Allyl chloride | | | 100 A | 20 A | |
| Aminobenzene acid (p-) | | | 20 A | 20 A | |
| Ammonia, anhydrous | | | 120 A | 20 A | |
| Ammonia, aqueous, 10% | A | A | A | A | |
| Aniline | | | 20 A 50 B | 80 A | PVDF: after 50 d, 75% strength remaining |