15. Material–Environment Interactions

There is no usage of materials without interaction with the environment. Material–environment interactions are relevant for all types of materials, be they of inorganic or organic in origin. Interactions with the environment can cause damage to materials but also might lead to an improvement of materials properties (e.g. oxidative passivation of aluminium or patina formation on copper surfaces). Interactions with the environment might also occur prior to the usage of materials, i.e. in the production phase. For example, before steel can be used for manufacturing of metal products, iron ore has to be extracted and processed.

The impact of the environment on the processes of the *materials cycle* (Fig. 1.15) will be discussed in Sect. 15.1.1 of this chapter. An important material–environment interaction, especially for inorganic materials, is corrosion, which has already been addressed in Chap. 12. Also the biological impact on organic and inorganic materials can be manifold and are presented in Chap. 14. Environmental mechanisms that impair the functioning of organic polymeric materials – such as weathering, ultraviolet (UV) radiation, moisture, temperature and high-pH environments – are the topics of Sect. 15.1.2. The influence of materials on the indoor climate and measurement methods to characterize emissions from materials are treated

in Sect. 15.2. Fire exhibits a drastic impact on materials; methods to characterize the flammability and fire behavior of materials are discussed in Sect. 15.3.

15.1 Materials and the Environment

15.1.1 Environmental Impact of Materials

The flow of materials has a significant global impact on the environment. Whereas at the beginning of the 20th century approximately 40% of the materials flow was attributed to renewable resources such as wood, fibres or agricultural products, this fraction dropped to only 8% by the end of the century [15.1]. The enormous increase in materials consumption within the United States is displayed in Fig. 15.1. The materials with the highest consumption rate are construction materials

(sand, gravel, stones, cement) and fossil fuels (oil, gas, coal). Other categories selected for Fig. 15.1 are minerals (clay, bauxite, phosphate rock, salt), iron and steel, wood and agricultural products (with 5 Mt in 2000 not visible in the diagram). Wood and products from agriculture and fishery are the only renewable resources from this point of view. All data are derived from the US Geological Survey [15.2]. The pattern of consumption is steadily increasing with some major historical events visible in the chart (World Wars I and II, the depression in the 1930s, the oil crisis in the mid 1970s
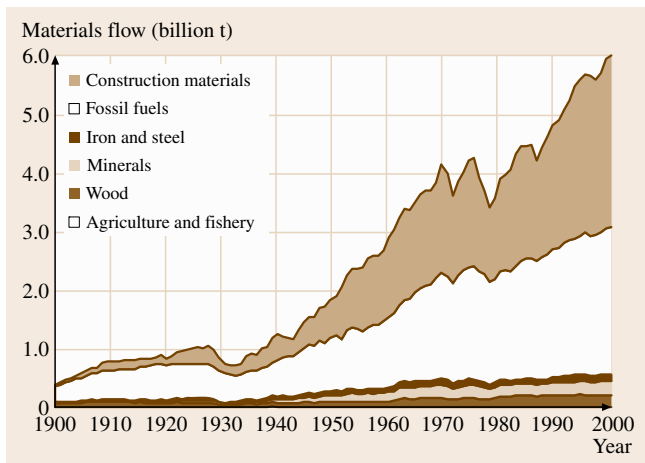
Fig. 15.1 Consumption of selected materials in the United States from 1900 to 2005 (after [15.2]). See text for material categories
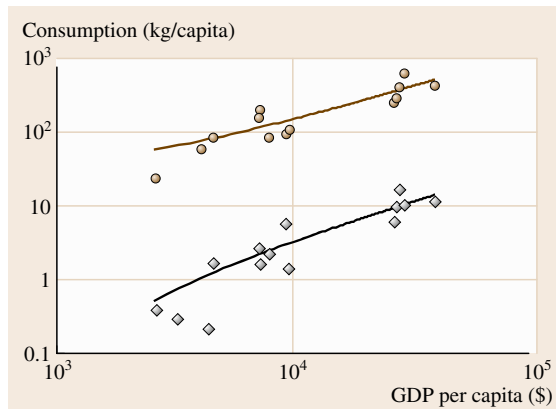

Fig. 15.2 The consumption of steel (*circles*) and copper (*diamonds*) per c.p.t. as a function of the gross domestic product per c.p.t. (after [15.3])

and later recessions). The figures suggest that the materials consumption per c.p.t. has increased by a factor of 6 from 2 t to 20 t per c.p.t. [15.1].

The environmental impact of materials usage is not easy to quantify. However, there are expressions which display the driving forces of this impact. *Graedel* and *Allenby* [15.4] describe the environmental impact as the product of population, gross domestic product (GDP) per person and environmental impact per unit of per c.p.t. GDP

$$
\begin{aligned}
&\text{Environmental impact} \\
&= \text{population} \times \frac{\text{GDP}}{\text{person}} \times \frac{\text{environmental impact}}{\text{unit of per c.p.t. GDP}} \, .
\end{aligned}
\tag{15.1}
$$

Population, the first term in (15.1), is still increasing globally. However, the population in most industrialized countries is more or less stable. GDP per person is a criterion for prosperity and varies from country to country. The general trend is positive. The last term in the equation is strongly technology-related. From (15.1) it is obvious that the production of materials using more efficient technologies and less waste production might lead to a reduced environmental impact if the effect of the first two terms can be compensated for. The fact that materials consumption is a function of the GDP per c.p.t. is shown exemplarily for steel and copper in Fig. 15.2.

The technology-related term, environmental impact per unit of per c.p.t. GDP, is the reciprocal value of the efficiency. One possibility to quantify the efficiency of materials production is to estimate the specific

energy consumption (SEC), i.e. the consumption of energy per mass of material produced. The world's SEC for steel has dropped significantly by almost 75% from 46 to 12 GJ/t since 1950 [15.5, 6]. However, the world production of steel is more than 400% of that in 1950 (1950: 190 Mt/a, 2000: 848 Mt/a [15.2]) and increased even more to 1351 Mt/a in 2007 [15.7]. Thus, the global energy consumption for steel production, i.e. the product of global production and SEC, increased from 8750 to 16 000 PJ/a. The environmental impact is directly related to energy consumption (e.g. consumption of fossil fuels, emissions etc.). As a result the environmental impact of steel production has increased, although the figure representing the technology term reduced to ≈ 25% of the initial value.

Specific energy consumption for the production of a certain material is only one part of the total impact of materials production on the environment. The concept of total material requirement (TMR) is an attempt to quantify the environmental impact of materials. TMR is the sum of domestic and imported primary natural resources and their hidden flows [15.8]. Hidden flows are often not considered in environmental analyses because they are attributed with no cost. However, overburden from mining, earth-moving for construction and soil erosion are major sources of ecological damage. The concept of TMR is exemplarily shown in Fig. 15.3 for the production of steel. From mined minerals to the final products a series of process steps takes place (exploration, mine-site development, extraction, milling, washing, concentration, smelting, refining, fabrication),

Table 15.1 The TMR of some metals, minerals and fuels

Material	TMR (t/t material)	Global production (t)	TMR (Mt/a)	References
Sand and gravel	1.18	8 000 000 000	9440	[15.10]
Hard coal	2	3 740 000 000	8826	[15.10]
Phosphate	34	130 000 000	4420	[15.10]
Gold	1 800 000	2445	4401	[15.9]
Crude oil	1.22	3 485 000 000	4252	[15.10]
Copper	300	12 900 000	3870	[15.9]
Iron	5.1	571 000 000	2912	[15.9]
Silver	7500	160 000	1200	[15.9]
Uranium	11 000	45 807	504	[15.9]
Lead	95	2 980 000	283	[15.9]
Platinum	1 400 000	178	249	[15.9]
Aluminum	10	23 900 000	239	[15.9]

each step is connected to other input flows such as energy or other resources. The run-of-mine coal and the mined iron ore are the hidden flows within this example. The hidden flows for metals related to metal-ore mining have been investigated by *Halada* et al. [15.9]. Table 15.1 lists the data for some metals, together with the data for some minerals and fuels.

The TMR in the United States in the 1990s was 80–100 t per c.p.t., in the European Union (EU-15) it was approximately 50 t per c.p.t. [15.11]. Although the TMR concept is widely accepted, there are no economic incentives to reduce TMR. However, attempts have been made to lower the environmental impact without reduction of economic wealth. Many companies evaluate the eco-efficiency of their products. Eco-efficiency is defined as the ratio of economic benefit per environmental and resource impact [15.12]

$$\text{Eco-efficiency} = \frac{\text{Benefits}}{\text{Costs}}$$
$$= \frac{\text{Economic benefit of good or service}}{\text{Environmental and resource impacts}} \; . \quad (15.2)$$

The objective is to maximize environmental and economic benefits and reduce both environmental and economic costs. That this approach is advantageous for the economy is supported by numerous examples from industry [15.13]. The concept of ecomaterials (ecomaterials = environmentally conscious materials) was developed in Japan and follows a similar direction [15.14]. Ecomaterials are defined as materials with green environmental profile, hazardous substance-free materials, recyclable materials and materials with high material efficiency. All four types of ecomaterials lead to a reduction in TMR and thus higher eco-efficiency.
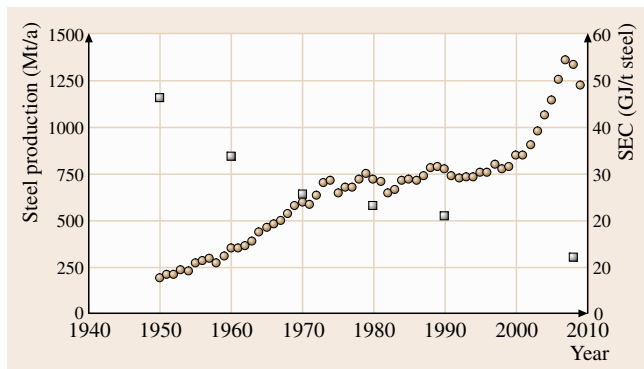
Fig. 15.3 Global steel production and specific energy consumption (global average) for the production of steel since 1950 (*circles* – steel production (Mt/a), *squares* – SEC (GJ/t steel)
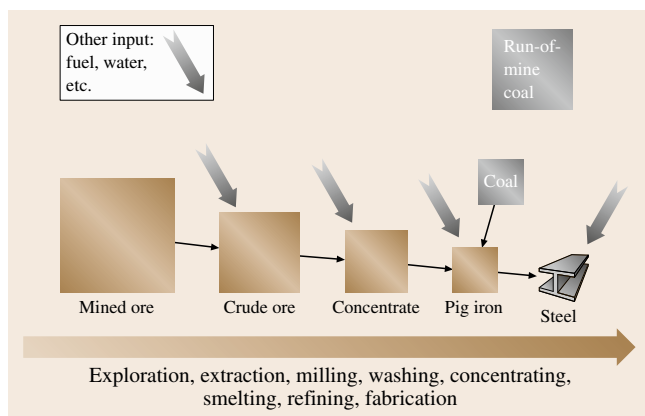

Fig. 15.4 The concept of TMR. The *brown boxes* are regarded as the hidden flows and account for the estimates of TMR. The sizes of the boxes are not to scale

15.1.2 Environmental Impact on Polymeric Materials

Relevant Environmental Factors

In chemistry, a differentiation is usually made between inorganic and organic matter. This discrimination is not an arbitrary one but rather reflects the completely different nature of the two. While the corrosion of metals as the economically most important environmental impact on inorganic matter has already been dealt with in Chap. 12, this subsection will look exclusively at polymeric materials. The latter not only present the most important sector of organic material but also exhibit an abundant variety of reactions and in general complex reaction behavior.

For (technical) polymeric materials, some special environmental factors are of basic relevance. Bond energies of a few eV (the solar UV comprises the range $3.1-4.1$ eV) make them sensitive to UV radiation, which makes weathering resistance a basic topic for polymers. Other relevant environmental factors will be only shortly discussed here.

Ageing – all the irreversible physical and chemical processes that happen in a material during its service life – often limits the serviceable lifetime to only a few years or even months. Thermodynamically, ageing is an inevitable process, however its rate ranges widely as a result of the different kinetics of the single reaction steps involved. Ageing becomes noticeable through changes of different properties, varying from from slight loss in appearance properties to total mechanical–technical failure. Ageing is mostly associated with a worsening of material properties, but sometimes it can also result in an improvement of properties, e.g. UV hardening.

Relevant environmental factors for the ageing of polymers are

1. solar radiation (see *weathering exposure* in the following),
2. heat,
3. chemical environment,
4. mechanical stress,
5. ionizing radiation,
6. biological attack.

Heat. Because of their low bond energies technical polymers can only be used in a limited temperature range [15.15]. Polyvinylchloride (PVC) for instance is only suited for permanent use up to $70\,°C$, polycarbonate (PC) up to $115\,°C$.

Thermal properties in general are dealt with in Chap. 8.

Chemical Environment. Exposed to water some polymers, like polyamides (PA), polyester, polyurethane, can be hydrolized, the mechanism for which may depend on acidity. Other polymers show a high sensitivity to atmospheric pollution, e.g. polyamides and polyurethanes even at room temperature are attacked by SO_2 and NO_2.

Akahori [15.16] used exposure to neutral oxygen radicals, produced by a plasma generator, for accelerated ageing tests.

Mechanical Stress. In the case of mechanical exposure, free radicals can be formed by rupturing chemical bonds, which is used as the initiation step in stress chemiluminescence [15.17].

Ultrasonic degradation can be used to produce polymers with a definite molecular size [15.18] or to degrade polymeric waste products. Frequent freezing/thawing cycles may also lead to degradation of dissolved polymers.

Ionizing Radiation. The impact of high-energy radiation (γ-, x-ray) leads to degradation and/or crosslinking [15.19]. In the presence of oxygen, degradation predominates.

Biological Attack. Not counting the mainly mechanical attacks of rodents or termites, microorganisms – such as mildew, algae and bacteria, that colonize their surfaces – can damage polymeric materials. Damage mechanisms vary for different polymers [15.20]. The microorganisms may attack in a direct way by breaking chemical bonds, or can act indirectly, e.g. increasing the migration of stabilizers. Producing their own pigments they can also disturb the appearance of the surfaces by color change.

In contrast with protecting polymeric materials from biological attacks (biocides) the opposite strategy is followed in sensitizing polymers to biodegradation for recycling.

Chapter 14 deals with the biogenic impact on materials in general.

Often the combined action of these environmental factors, which occur as synergistic or antagonistic effects, has to be considered.

Weathering Exposure

Ageing of polymeric materials by the impact of weathering is mainly initiated by the action of so-

lar radiation. However, other climatic quantities such as heat, moisture, wetting and ingredients of the atmosphere, influence the photochemical ageing and are answerable for the final ageing results. To date there are no satisfactory general answers to the questions of the accurate mechanisms of the photooxidation and photodegradation of pure polymers, not to mention technical polymeric materials.

General Principles of Photoinitiated Ageing. From a theoretical point of view, pure aliphatic polymers show no absorption in the spectrum of solar radiation. For example, the UV absorption bands of pure polyethylene, which contains only C−C and C−H bonds, are located at wavelengths below 200 nm. Only polymers with aromatic groups or conjugated double bonds absorb natural solar UV radiation. For this reason, many polymers should be capable of withstanding the action of solar radiation during outdoor exposure.

The spectral response of a property change of a polymer in the solid phase does not coincide with its absorption spectrum in the spectral range of solar radiation. Even in many aromatic-type polymers, the absorption of radiation, which is responsible for the initiation of ageing, takes place through chemical irregularities or impurities. These originate either during the polymerization process and the processing of the polymers or are residues of catalysts. These chromophores, which are capable of absorbing the UV portion of terrestrial solar radiation, are unavoidable in technical polymers. *Menzel* and *Schlüter* [15.21] for example describe an increase of absorption at wavelengths above 300 nm and a decrease of weathering resistance after multiple processing of PVC.

Photoinitiated ageing of polymeric materials can be caused

1. directly via an excitation of a molecule in a non-binding state that leads to photolytic chain scission (dissociation);
2. indirectly via an excitation of a molecule in a bound singlet state S_x that can be deactivated by several reaction paths, e.g. an oxidative reaction of the exited polymer molecule with O_2.

The multistage processes of photoageing can be illustrated by the rough scheme in Fig. 15.5, which shows the levels of the exited states of an organic molecule A. The levels S_1 and S_2 (singlet states) and T_1 and T_2 (triplet states) are the most important energy levels in photochemistry. The thin lines above these levels indicate the vibrational and rotational levels. The nearly ver-
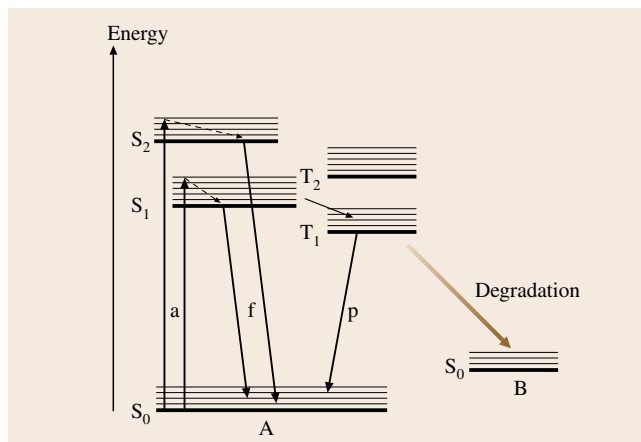

Fig. 15.5 Scheme of the energy levels and transfers in an organic molecule, a – absorption, f – fluorescence, p – phosphorescence and photochemical degradation

tical solid arrows indicate the absorption and emission of radiation, the dashed arrows show radiationless energy transfers. The main processes are described below.

1. Absorption of radiation is the initiating photophysical reaction. At room temperature the polymer molecule A is in the ground state S_0. By the absorption of a photon, it is transferred from the ground state S_0 to the exited state S_1 (including vibrational and rotational levels) and, at a higher photon energy, also to the exited state S_2. Under conditions of natural and artificial weathering, the absorption of radiation can be considered as largely independent of any external influences.
2. This is followed by deactivation of exited states. The electronically exited states are no longer in a thermal equilibrium and try to transfer the absorbed energy within a very short time. This deactivation takes place by several competing processes:
   a) Intramolecular deactivation. This energy transfer takes place from the exited state S_1 by fluorescence, or after internal conversion, intersystem crossing and relaxation from higher vibrational energy levels from the exited state T_1 by phosphorescence. This type of deactivation does not change the polymer molecule.

      Therefore, the absorption of radiation is not a sufficient condition for an ageing process. Even if the absorbed energy is high enough to rupture a bond, the energy has to be accumulated in this bond.

b) Intermolecular deactivation. This also takes place from the exited states S_1 and T_1 by radiative and radiationless transitions to an acceptor. This energy transfer plays an important role in photostabilization and even the photosensitization of polymers.

c) Deactivation by chemical reactions. In a nonbinding electronically exited state, the weakest of the bonds involved dissociates into two radicals. These reactive intermediate pieces can recombine or react with many other molecules to form stable final products.

For a comprehensive survey of the photochemistry of polymers see, e.g., *Calvert* and *Pitts* [15.22] or *Ranby* and *Rabek* [15.23].

This short and superficial representation of the complex reaction processes during photochemical ageing gives an idea of the numerous factors that can influence photoinitiated ageing at many stages. These influences on the ageing behavior of polymers can only be roughly predicted by means of theoretical considerations. Quantitative results on the influence of the different climatic quantities have to be determined by experiments.

To interpret the results from artificial weathering tests, it is necessary to have an idea of the influences of the different climatic quantities on photochemical ageing. This paper summarizes some results of investigations on the spectral response of polymers and on the influence of heat, moisture, the style of wetting, acid precipitation and biofilms on ageing results.

Spectral Response of Polymers. The spectral response of polymers is usually expressed in terms of their spectral sensitivity or activation spectrum, which unfortunately are not used consistently in literature. Data on the spectral response of polymers can be obtained in principle by two methods

1. A direct method, where the effect of a wavelength of radiation is determined by irradiation with a small spectral band or line of radiation with known irradiance. This technique determines the spectral sensitivity (or wavelength sensitivity), see *Trubiroha* [15.24, 25].

2. An indirect method, which ascribes the incremental property change measured behind a pair of filters to the incremental (UV) radiation of a radiation source transmitted by the shorter-wavelength filter of the pair. This technique, the so-called filter technique, is used to determine the activation spectrum of a polymer, described in full, e.g., by *Searle* [15.26].
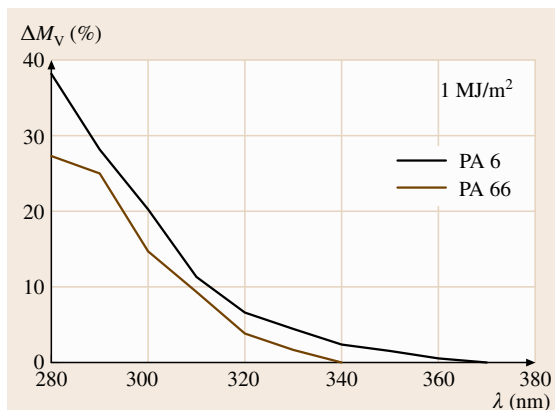

Fig. 15.6 Spectral sensitivity of polyamides, change in molar mass M_v as a function of wavelength of irradiation
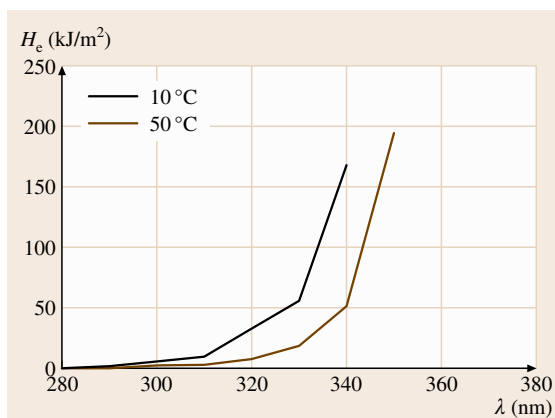

Fig. 15.7 Spectral sensitivity of polycarbonate at 10 and 50 °C. The graph shows the radiant exposure H_e, necessary to produce a 10% loss in internal transmittance as a function of the wavelength of irradiation

Spectral Sensitivity (or Wavelength Sensitivity). Spectral sensitivity data can be obtained by

1. observing the changes of a polymer property as a function of an equal radiant exposure with nearly monochromatic radiation at different wavelengths,

2. observing the radiant exposure with nearly monochromatic radiation, necessary to produce a defined change of the polymer property, if the change of the property is not linearly dependent on the radiant exposure.

The spectral sensitivity of the decrease of molar mass of additive-free polyamide films with a thickness of about $40 \, \mu m$ is illustrated in Fig. 15.6. The

changes were normalized for an equal radiant exposure of $1 \, MJ/m^2$ at each wavelength in the spectral range 280–380 nm. The figure shows the decrease of the molar mass M_v of the two polyamides PA 6 and PA 66 with wavelength of irradiation. The change of M_v was linearly dependent on the radiant exposure in the investigated range.

PA 6 was more sensitive than this PA 66. The sensitivity of molecular degradation increases strongly with decreasing wavelength. Molecular degradation of the PA 6 film was only sensitive to wavelengths shorter than 370 nm. The PA 66 film only degraded at wavelengths below 340 nm.

The spectral sensitivity of the yellowing of a PC film with a thickness of 0.7 mm specimen temperatures of 10 and 50 °C is shown in Fig. 15.7. Because the yellowing of PC is not linearly dependent on the radiant exposure the figure shows the radiant exposure H_e which is necessary to reduce the internal transmittance of the PC film at 360 nm by 10%. With increasing wavelength higher radiant exposures are required to produce this defined change of internal transmittance. With increasing temperature the curve shifts to longer wavelengths by about 10 nm, when the temperature rises from 10 to 50 °C, which means that the spectral sensitivity increases with increasing temperature.

Activation Spectrum. The activation spectrum is the polymer spectral response data measured using the filter technique and is specific to a defined type of radiation source and a fixed exposure time.

An example of the calculated activation spectrum (AS) of the PA 6 film with a thickness of 40 μm mentioned above to solar global radiation E_{glob} and the spectral sensitivity (SS) are given in Fig. 15.8. A simplified qualitative definition of an activation spectrum is the superimposition of the spectral sensitivity (SS) of a property change of a test specimen onto the spectral irradiance $E_{e\lambda}$ of a given radiation source. At short wavelengths the activation spectrum must be zero where the spectral irradiance of the radiation source is zero; at long wavelengths the activation spectrum must be zero where the spectral sensitivity is zero. Therefore, information on an activation spectrum needs to be accompanied by information on the spectral irradiance of the radiation source.

Many other unstabilized and stabilized polymers show no remarkable response to radiation of wavelengths above 400 nm [15.24, 26]. However, investigations of very light-sensitive papers by the National Institute for Standards and Technology (NIST) [15.27]
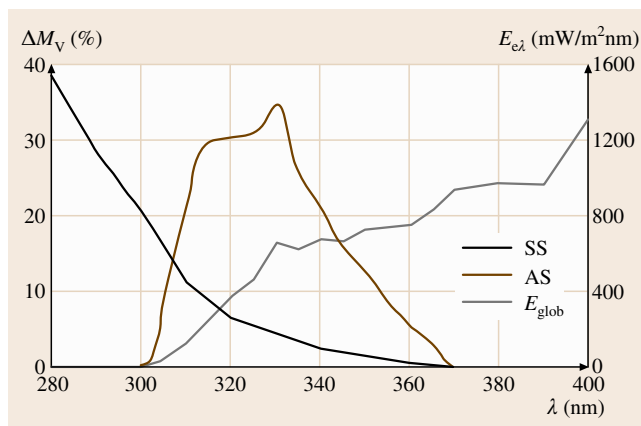

Fig. 15.8 Polyamide 6 film: spectral sensitivity (SS) and activation spectrum (AS) at solar global radiation E_{glob}

and of TiO_2-pigmented polymers and paints by *Kämpf* and *Papenroth* [15.28] ascertained a slight response to wavelengths up to about 450 nm. Only very light-sensitive color pigments fade strongly on exposure to visible radiation.

These experimental determinations of the spectral response of polymers have to be considered as typical results that can be influenced for example by the temperature, the degree of crystallinity and the thickness of the specimen or the duration of exposure, not to mention additives and pigments, which can be photostabilizers or photosensitizers, see *Trubiroha* et al. [15.29].

Irradiance Level. Besides the wavelength, the irradiance level during exposure may also have an influence on the degradation behavior of transparent test specimens.

Figure 15.9a shows the decrease of radiant flux in a clear transparent film for three different values of the product μd (absorption coefficient × thickness of a film/sheet) in relative units. If the photochemical ageing only depended on the absorbed energy, the ageing results (Fig. 15.9b) would run parallel to the curves of radiant flux in the film, calculated according to $E = E_0 10^{-\mu d}$.

Figure 15.9b illustrates schematically the changes of carbonyl concentration in a low-density polyethylene (PE-LD) sheet with a thickness of 3 mm as a function of depth at different partial pressures of oxygen, measured by *Furneaux* et al. [15.30]. In a pure oxygen atmosphere, the change of the carbonyl index (infrared (IR) absorption region of the oxidation products) runs parallel to the decrease of radiant flux. However, the radiation exposure in air shows a strong formation of carbonyl groups at the
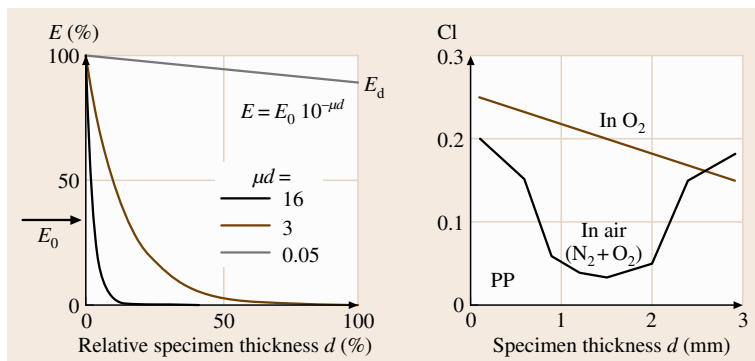
Fig. 15.9 (a) Radiant flux in a transparent sheet, **(b)** change of carbonyl index (CI) in a low-density polyethylene sheet with depth and partial pressure of oxygen

two surfaces of the sheet. In the specimen's core thickness of 1 mm only very low carbonyl concentrations could be found. The rate of photooxidation definitely depends on oxygen diffusion, and thereby on the irradiance level, which implies an indirect dependence on the specimen temperature.

Photodegradation: Influence of Heat. Increased temperatures do not only increase diffusion rates but generally most chemical reactions. Figure 15.10 shows the loss of gloss of a white TiO_2-rutile-pigmented paint with a binder system consisting of linseed oil/alkyd as a function of the temperature of the specimen surface. It shows the decrease of the reflectometer value at 20, 35, and 50 °C, with time of weathering exposure. With increasing temperature, there is an increasing loss of gloss.

The strong dependence of many photodegradation reactions on the specimen temperature explains why it was not successful to establish a weathering station high
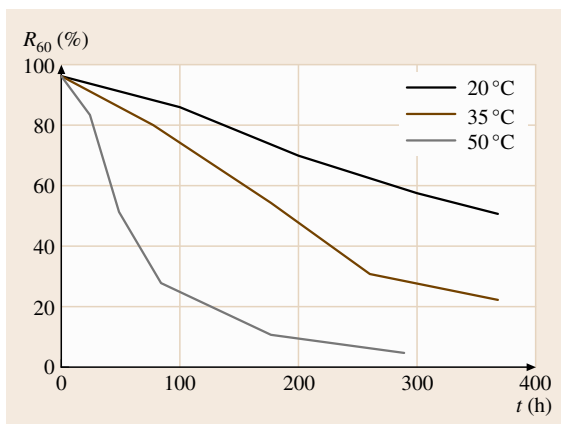

Fig. 15.10 Loss of 60° gloss of a paint with exposure duration t and specimen temperature

in the Alps, although there is a higher level of UV radiation. The mean temperature was about 20 °C lower than in weathering stations at sea level. Even *Boysen*'s attempts to combine the natural weathering under daylight with artificial UV exposure during the night did not show the estimated acceleration due to the influence of temperature [15.31]. The low temperature of the specimen surfaces in the night with artificial irradiation changed the ageing processes.

It has to be mentioned here that the increase of surface temperature by irradiation can be different under natural and artificial irradiation, depending on the source of radiation and the color of the specimen. This temperature difference influences the acceleration factors for specimens with different colors.

Photodegradation: Influence of Moisture and Wetness. For unpigmented translucent PVC no dependence of the discoloration in the range of relative humidities between 10 and 90% RH could be found. However, the yellowing of white TiO_2-rutile-pigmented PVC used for window frames, which occurred as a weathering effect, showed a strong dependence on the relative humidity during irradiation [15.32].

Figure 15.11 shows the discoloration of eight specimens of PVC frames with different stabilizers and modifiers expressed in color differences ΔE corresponding to the grades of the greyscale after UV radiant exposure of about 190 MJ/m^2 at 50 °C. The discoloration in the moist climate was much lower than in the dry climate. This effect can be explained by the photoactivity of TiO_2 at high relative humidity, which destroys the polyene sequences in PVC.

The influence of relative humidities of 10 and 90% RH in the temperature range from 0–50 °C on the photodegradation of PA 6 is shown in Fig. 15.12. The figure shows the changes of molar mass M_v after UV

radiant exposure of about $3.5\,MJ/m^2$. With increasing relative humidity and temperature, increasing degradation can be seen. In the temperature range 20–40 °C a stronger increase of the dependence, which probably correlates with the change of the glass-transition temperature, can be observed.

In contrast to *Matsuda* and *Kurihara* [15.33], who observed a strong influence of moisture content on changes of mechanical properties of PE-LD during weathering, *Löschau* and *Trubiroha* [15.34] could not confirm this result in the 1970s with three different PE-LD samples. Investigations with different high-density polyethylene (PE-HD) films however, showed a distinct influence of moisture on the changes of mechanical properties, decrease of molecular mass and the formation of carbonyl groups. After UV radiant exposure of $13\,MJ/m^2$ in a Global UV-Test device at 40 °C and relative humidities of 20, 55 and 95%, the carbonyl index increased from 0.6 at 20% RH to 2.5 at 95% RH; the decrease of molar mass increased from 14% at 25% RH to 23% at 95% RH.

From these results, one cannot conclude that the photooxidation of PE-HD is dependent on moisture in contrast to PE-LD. The PE-LD was a pure polymer whilst PE-HD contained additives.

Other important parameters may be the type of wetting, e.g. dew or rain, and the duration of the wetness of the wet–dry cycles, which can cause mechanical stresses during the absorption or desorption of water.

Photodegradation: Influence of Atmospheric Acid Precipitation. Investigations on atmospheric precipitation show that rain with a pH of 2.4–5.5, fog with a pH of 2.2–4.0 and dew with a pH ≥ 2.0 are not rare phenomena, and not only observed in industrial regions. Acid atmospheric precipitation is formed when specific pollutants combine with water or dust particles in the atmosphere. By far the largest contribution to this problem arises from sulphur dioxide SO_2, a by-product of fossil-fuel combustion. In the atmosphere, SO_2 concentrations of up to 1 ppm are no rarity during the morning rush hours with the increased use of heating systems. When oxidized to sulphuric acid, H_2SO_4, it accounts for 62–79% of the acidity of rain. Most of the remaining acid is from nitrogen oxides NO_x, found mainly in automobile exhaust fumes, which are oxidized to nitric acid HNO_3 (15–32%). In addition to these two main species, hydrochloric acid HCl (2–16%), also produced by burning coal, is found in the atmosphere [15.35].

However, rain, dew, fog and dust with pH ≥ 2.0 are not the final forms of the acid precipitation which can
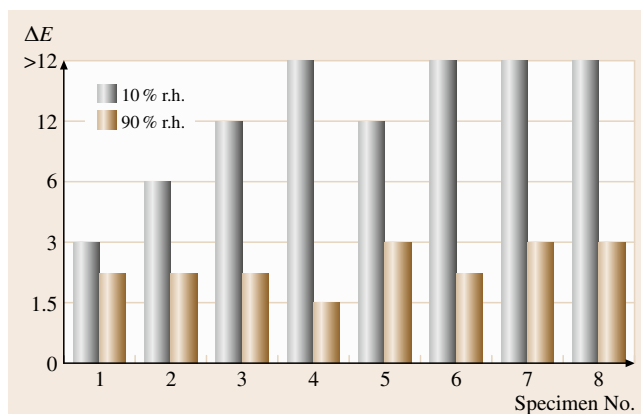
Fig. 15.11 Weathering-induced discoloration ΔE of white polyvinylchloride at low and high relative humidity
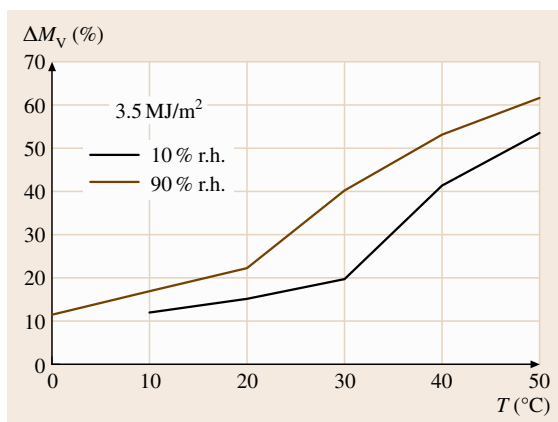
Fig. 15.12 Photodegradation of polyamide 6 with temperature and relative humidity after UV radiant exposure of about $3.5\,MJ/m^2$, where M_v is the molar mass

act on surfaces of polymeric materials. Following the vapor–pressure curves it can be stated that the acid precipitation will concentrate up to about 70% sulphuric acid on hot and inert surfaces by the evaporation of H_2O, HNO_3 and HCl. A summary of the influence of acid precipitation on different polymers has been published [15.36, 37]. Hindered amine light stabilizers can be another weak point of technical polymeric materials [15.38].

Results generally show a synergetic effect of acid precipitations with UV radiation which accelerates the effect of artificial weathering tests, but there are also hints that the ageing processes of some polymers, e.g. unstabilized PE and PC, can also be slowed down by acid precipitations.

Photodegradation: Influence of Biofilms. Any surface of a material has a biofilm. This biomaterial or products of their metabolism may also have a synergistic effect on the weathering behavior of polymeric materials, e.g. the mildew growth that causes pinholes in automotive coatings, especially in warm and humid climates like in South Florida. An attempt to produce the formation of these pinholes by means of standardized laboratory mildew tests that did not incorporate radiation failed [15.39].

Dragonflies that confuse a glossy clear coat with a water surface lay their eggs on this surface. Because of heating by solar radiation and the photochemical action of UV radiation, these eggs will be destroyed. *Stevani* et al. have demonstrated that the degradation products can hydrolyze acrylic/melamine resins that are in common use for clear coats [15.40].

Photodegradation: Influence of the Prior History of Test Specimens. *Menzel* and *Schlüter* [15.21], see above, described a decrease of weathering resistance after repeated processing of PVC. Similar results were obtained by *Chakraborty* and *Scott* for PE-LD [15.41].

This means that results from weathering, as well as being influenced by climatic quantities, may also be affected by the prior history of the exposed specimen (surface), for example by the quality of the specimen surface. Figure 15.13 demonstrates the influence of surface roughness on the discoloration of a white specimen of an extruded PVC window frame. By artificial irradiation in a dry climate, dark brown stripes develop over some areas, where the unexposed specimen showed a reduced gloss from processing.

Drying conditions of a coating may influence its ageing behaviour different loss of stabilizer. An increase of the degree of crystallinity of polyamide by annealing can increase its stability. Therefore, different prior his-
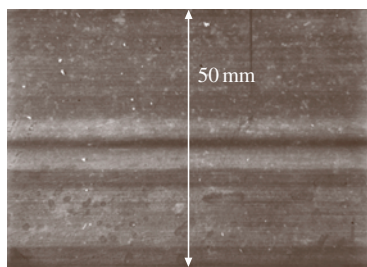

Fig. 15.13 Effect of surface roughness on the discoloration of a white polyvinylchloride specimen. Surface areas that were originally glossy show a light color change, surface areas that were dull show a strong dark brown color

tory of test specimens are often the cause of varying weathering results.

Natural Weathering. In practice, many polymeric materials are exposed to the whole variety of climatic conditions in the world. High levels of UV irradiance, annual UV radiant exposure, temperature, and humidity are extreme conditions for most polymeric materials. However, depending on the anticipated market of the polymer product, other exposure conditions may be important, e.g. maritime exposure to salt spray.

Corresponding to the variety of climates that are a result of latitude, altitude, and special geographical conditions, there are numerous natural-weathering sites across the world.

Benchmark climates for natural-weathering tests are the warm and humid, subtropical climate in Florida and the hot and dry, desert climate in Arizona, see *Wypych* [15.42].

At a given exposure site the real action of weather conditions can be varied by different exposure angles from the horizontal to vertical, by exposure under glass, by sun-tracking exposure or by Fresnel solar concentrators.

The following considerations have to be taken into account

1. It is very difficult to really reproduce results from an outdoor exposure in weathering devices, because the outdoor exposure results vary for different locations, e.g. outdoor exposures at geographical locations such as Florida or Arizona, which accelerate the ageing of polymers compared to Europe, do not duplicate the ageing results of outdoor exposures in Europe. Even at one geographical location, the weather conditions of a season or a year, and therefore the ageing results, are not repeatable within a manageable time.
2. Any accelerated test, either artificial or outdoor, is only an approximation to the exposure stress in the field.

Artificial Weathering. To estimate the service life of products made from polymers or for the development of more stable polymers, the conditions of outdoor exposure are simulated in accelerated artificial-weathering devices. These machines were introduced in 1918, but a long period of time was required for the development from the first purely artificial radiation sources equipped with a carbon arc to artificial weathering devices. In the course of time, these devices have become

good simulators of the actinic portion of the solar radiation. This means that there may be a good simulation of the first photophysical reaction of photochemical ageing in these machines. The other climatic quantities of the weather can never be simulated perfectly due to time compression or acceleration; for this reason, deviations can influence the ageing result and affect the correlation with results from outdoor exposures.

There are a number of different concepts for these weathering devices

1. Devices equipped with xenon arc lamp(s). These machines show good simulation of the maximum of spectral irradiance in the UV and visible (Vis) range of terrestrial solar radiation at vertical incidence of direct solar radiation.
   The main advantage of these devices is that even very light-sensitive materials, i.e. sensitive to Vis radiation, can be investigated. The main disadvantage is the high thermal charge to the specimen surfaces by Vis and IR radiation, which makes conditioning of the surfaces at low temperatures and high relative humidity during irradiation impossible.
2. Devices equipped with fluorescent UV lamps. These machines show good simulation of the actinic portion of terrestrial solar radiation with fluorescent type 1 (340) UV lamps and a combination of different types of fluorescent UV lamps.
   The big advantage of these devices is their low energy consumption and a very low thermal charge to the specimen surfaces by Vis and IR radiation. Therefore, irradiated surfaces of specimens can be easily conditioned over wide temperature and relative humidity ranges. However, there are some limitations concerning lightfastness tests of specimens that are very sensitive to visible radiation.
3. Devices with carbon arc(s). These machines show a spectral distribution of irradiance that differs strongly from that of terrestrial solar radiation. Additionally there is the same disadvantage as for xenon-arc machines: a high thermal charge to the specimen surfaces by Vis and IR radiation

These machines are mainly used in the Asian market.

Weathering Standards. There are hundreds of national and international standards and company specifications that prescribe exposure conditions for artificial and outdoor weathering exposure tests considering usual and specific conditions, e.g. in the automotive industry or for roofing materials.

Most of these tests procedures are based on the following International Organization for Standardization (ISO) standards

- for the natural exposure of plastics: ISO 877 Plastics – methods of exposure to solar radiation (Part 1: General guidance, Part 2: Direct weathering and weathering using glass-filtered solar radiation, Part 3: Intensified weathering using Fresnel mirrors);
- for paints and varnishes: ISO 2810 Paints and varnishes – natural weathering of coatings – exposure assessment.
- artificial exposure procedures are described for plastics in: ISO 4892 Plastics – methods of exposure to laboratory light sources, parts:
  a) general guidance,
  b) xenon-arc sources,
  c) fluorescent UV lamps,
  d) open-flame carbon-arc lamps,
- and for paints and varnishes in: ISO 11341 Paints and varnishes – artificial weathering of coatings and exposure of coatings to artificial radiation alone – exposure to filtered xenon-arc radiation (09.94); and ISO 11507 Paints and varnishes – exposure of coatings to artificial weathering – exposure to fluorescent UV and water.

Some failures of polymeric materials from outdoor exposure may not be able to be reproduced in artificial-weathering devices using standard weathering conditions. In these cases, it may be necessary to deviate from the standard conditions.

Determination of Property Changes. Before a property change due to environmental impact can be detected, it is of the outmost importance to characterize the material to be exposed as thoroughly as possible in the unexposed state. It has to be taken into account that the production process of the material might already have resulted in a heterogeneous material in regard to its properties on the surface compared to the bulk.

In most cases, an environmental impact on a material first affects its surface before it accumulates and spreads over the bulk of the material. This brings up two consequences for the determination of property changes: especially in the early stages of an environmental impact a heterogeneous distribution of property changes between the surface and bulk will result [15.43] and secondly, the first effects of weathering will be able to be detected by surface-emphasizing detection techniques.

Generally, weathering-induced degradation will start on a molecular level. For instance impurities in the material or external contamination with highly reactive secondary molecules can cause an increased reactivity in this region and act as the starting point of the degradation process, which can then spread like an infection until ultimately the whole bulk of the material is affected by the degradation process [15.43]. This means that detection techniques for weathering effects that are able to detect changes on a molecular level have the potential to detect the earliest stages of a degradation process.

Guidance for the determination of property changes of general interest is given for plastics by ISO 4582 (Plastics – determination of changes in color and varia-

tions in properties after exposure to daylight under glass, natural weathering or laboratory light sources) and for paints and varnishes by ISO 4628 (Paints and varnishes – evaluation of degradation of coatings; designation of quantity and size of defects, and of intensity of uniform changes in appearance), Parts 1–10.

A number of detailed techniques for the investigation of individual property changes are described in separate standards. Common testing procedures of effects of environmental impacts and – as far as they exist – their respective standards can be found in Table 15.2.

A review of the analytical techniques to look for the reasons for the observed changes can be found in *Kämpf* [15.44] and other references [15.45–49]. A number of these techniques are listed in the following.

Table 15.2 Common test procedures for property changes due to environmental impact on plastics, paints and varnishes

Property category	Individual property assessed	Standard
General	Mass	
	Dimension	
Appearance	Gloss retention	ISO 2813
	Light transmission	ISO 13468-1
	Haze	ISO 14782
	Blistering	ISO 4628-2
	Cracking	ISO 4628-4
	Flaking	ISO 4628-5
	Chalking	ISO 4628-6 (tape method)
		ISO 4628-7 (velvet method)
	Corrosion around a scribe	ISO 4628-8
	Filiform corrosion	ISO 4628-10
	Cracking or crazing	
	Delamination	
	Warping	
	Colorimetry, for instance yellowing	SO 7724-1
	Biofilm formation	
	Migration of components from inside to surface	
Mechanics	Tension (particular elongation at break)	ISO 527, all parts
	Flexibility	ISO 178
	Impact strength	
	Charpy impact strength	ISO 179-1, ISO 179-2
	Izod impact strength	ISO 180
	Puncture test	ISO 6603-1, ISO 6603-2
	Tensile impact strength	ISO 8256
	Vicat softening temperature	ISO 306
	Temperature at deflection under load	ISO 75, parts 1–3
	Dynamic mechanical thermal analysis	ISO 6721, parts 1, 3, and 5
Chemistry	Effect of immersion of sample in chemicals	ISO 175
	Chemical changes (such as the detection of oxidation products by infrared spectroscopy)	

Table 15.3 Analytical techniques that can be used for spot and surface analysis (see also Sect. 6.1, surface chemical analysis)

Acronym	Meaning	Principle/assessed property	Resolution	References
EMA	Electron beam micro-analysis	Excitation by electrons, emission of x-ray photons for elements boron to uranium. Applications: detection of inorganic inhomogeneities in polymeric materials	Lateral: $0.1-3\,\mu m$ (minimum 13 nm)	[15.50]
SEM + EDX	Scanning electron microscopy coupled to energy dispersive analysis	As above, but energy dispersive analysis instead of focusing wavelength dispersive analysis. For light elements slightly inferior spectral resolution and lower sensitivity than EMA	Lateral: $1\,\mu m$, Depth: $\approx 1\,\mu m$	[15.51, 52]
TEM	Transmission electron microscopy	Scattered and unscattered electrons are detected after excitation with electrons. In crystalline regions electron diffraction occurs	Lateral: $0.2-10\,\mu m$	[15.53]
LAMMA	Laser microprobe mass analysis	Excitation by photons. Laser light is focussed through a light microscope onto the sample, which is caused to evaporate. Emitted ions are detected in time-of-flight mass spectrometer. Detection limit better than $10^{-18}-10^{-20}$ g or concentrations in ppb range	Lateral: better than $1\,\mu m$ Depth: $> 0.1\,\mu m$	[15.54, 55]
ESCA (XPS)	Electron spectroscopy for chemical analysis (x-ray photoelectron spectroscopy)	Photoionization of electrons on inner atomic shells by characteristic x-ray irradiation. Quantitative identification of atoms, determination of bonding state, oxidation states, depth profiling, identification of polymers. Detection of inorganic or polymeric impurities on polymer matrix. Crude depth profiling possible by angle-resolved XPS (control of analyzer collection angle)	Lateral: $1-1000\,\mu m$. Imaging: e.g. $0.1-10$ mm Depth: $1-10$ nm	[15.56, 57]
AES	Auger electron spectroscopy	Emission of secondary electrons after excitation with x-ray. In combination with ablation by sputtering allows depth profiling	Lateral: $0.1-3\,\mu m$ Depth: $0.4-2.5$ nm	[15.58]
(TOF-) SIMS	(Time-of-flight) secondary ion mass spectrometry	Surface is sputtered with positively charged ions. Emitted particles are neutral as well as secondary ions; the latter are detected by means of mass spectrometry. Trace detection of polymers, composition of copolymers and polymer blends, detection of additives or contamination on polymer surfaces, determination of molecular mass	Lateral: $< 50\,\mu m$, (imaging SIMS: 200 nm), Depth: 1 nm	[15.59, 60]
XFA	X-ray fluorescence analysis	Excitation by photons, emission of photons. Applicable for trace detection of impurities at $10^{10}-10^{13}$ atoms/cm^2	Lateral: $1\,\mu m$	[15.61]
ATR-IR	Attenuated reflection infrared spectroscopy	Absorption spectroscopy with infrared radiation source. Sample is characterized using multiply attenuated reflection of IR between sample surface and totally reflecting crystal on top. Vibrational spectra allow qualitative and quantitative analysis of functional groups and render information on the constitution. Carbonyl bands can give measure for oxidative ageing	Lateral: ≈ 3 mm	[15.62]
Micro-IR	Micro-infrared spectrometry	Coupling of infrared spectrometer to microscope	Lateral: $1\,\mu m$	[15.63]
AFM	Atomic force microscopy	The force between the tip and the surface of the sample is monitored while scanning over it	Depth: 0.5 nm	[15.64]
LM	Light microscopy	Photons of visible light transmitted through, or reflected from, the sample material are depicted	Lateral: $\approx 1\,\mu m$	[15.65]

Part D | 15.1

Table 15.4 Analytical techniques allowing the investigation of bulk changes

Acronym	Meaning	Principle/assessed property	References
	Optical transmission spectroscopy (IR, Vis, UV)	Species are identified by the frequencies and structures of absorption, emission, or scattering features, and quantified by the intensities of these features. Enable trace analysis of organic additives such as heat and UV stabilizers, flame retardants, slip and deforming agents, solvent or monomeric or oligomeric residues, softeners	[15.66]
	Thermo-analytical techniques	Investigate a physical property of the sample as a function of a controlled temperature program. Increased analytical value by coupling to infrared or mass spectrometers, for instance TG-FTIR of TG-MS	[15.67]
AAS	Atomic absorption spectrometry	Atomized either by flame or electrothermally; AAS is characterized by selective resonance absorption of neutral atoms of the light of monochromatic light, proportional to its concentration	[15.68]
XFA	X-ray fluorescence analysis	Emission and detection of characteristic x-ray radiation of atoms after excitation by means of high-energy γ-ray Bremsstrahlung. Allows multi-element analysis. Semiquantitative analysis of inorganic components in polymers	[15.61]
ICP-MS	Inductively coupled plasma mass spectrometry	Ionization of a sample and separation of the ions in a mass spectrometer. Allows multi-element analysis. Remarkably lower detection limits (ppt range) than AAS. Only low concentration solutions usable	[15.69]
GPC	Gel permeation chromatography	The molar mass of polymers dissolvable in GPC solvents (most commonly tetrahydrofuran or chloroform) can be determined as retention time in chromatographic columns that work according to the size exclusion principle. Requires calibration of molar mass as function of retention time. Gives the complete molecular-weight distribution curve	[15.70]
CL	Chemiluminescence	Weak photon emission in first approach linear to reaction rate of oxidation reaction detected by for instance photomultipliers. Very sensitive means to follow oxidative ageing kinetics of polymers. Depending on transmission properties of the sample surface biased. No direct information on emitting species	[15.71–73]

Spot Analysis of Polymer Surfaces. The aforementioned spatial heterogeneous reaction of most interactions between polymeric materials and the environment implies the necessity for imaging microscopic techniques. These allow a distinctive analysis of spots within the bulk as well as the surface to be done.

Polymer Bulk Detection Techniques.
Changes in the Composition (Polymer–Copolymer–Additives–Fillers). The techniques listed under this topic also look at bulk properties but particularly allow conclusions to be drawn about the composition of a multicomponent system.

Limits of Lifetime Predictions. For lifetime predictions many industrial areas have already made the transition from strong dependence on long-term practical tests to strong reliance on short-term laboratory test results. In these cases the lifetime of the material mostly depends on the impact of only one or two, often relatively constant, exposure parameters, e.g. the temperature, that dominate the limitation of lifetime.

For polymeric materials exposed to natural weathering conditions lifetime predictions based on laboratory tests are much more complex. The results of property changes of polymeric materials as a consequence of

Table 15.5 Techniques particularly suited to determine changes in composition

Acronym	Meaning	Principle/assessed property	References
NMR	Nuclear magnetic resonance	Resonance interaction between the nuclear spins of, for instance, ^{1}H or ^{13}C atoms of the sample, which is placed in a homogenous external magnetic field, with high-frequency radio waves. Allows analysis of composition and structural changes, such as chain branching and stereochemical configuration. NMR is not sensitive enough for minor components	[15.74, 75]
IR	IR/Raman spectroscopy	Vibrational spectra allow qualitative and quantitative analysis of functional groups (kind and concentration) and render information on the constitution. Carbonyl bands can give measure for oxidative ageing	[15.76]
UV/Vis	UV/Vis micro-spectrophotometry	For depth profiling, typically microtome cross-section slices of the sample are investigated in transmission mode. Allows the detection of the formation or disappearance of chromophoric groups, such as degradation products of the polymer as well as additives	[15.77]
ESCA	Electron spectroscopy for chemical analysis	For the principles see Table 15.3. Applicable for depth profiling in combination with sputtering	Sect. 6.1.2
SIMS	Secondary-ion mass spectrometry	For principles see Table 15.3. Applicable for depth profiling in combination with sputtering	Sect. 6.1.3
Pyrolysis-MS	Pyrolysis mass spectrometry	A sample is pyrolized using heat, and the fractions are analyzed by a mass spectrometer to which the pyrolysis cell is coupled	[15.78]

accelerated artificial and long-term outdoor exposures may depend on

1. the specific material under test (e.g. polymer type, formulation, dimensions, processing conditions, the age and the initial moisture content of the test specimen at the start of exposure),
2. the exposure conditions (e.g. mean and maxima of the UV irradiance, temperature, relative humidity and time of wetness, acidic or biological attack, the season when outdoor exposure is started and when it is terminated), and
3. the type of analytical determination and evaluation of the property changes (e.g. physical or chemical properties, surface- or bulk-influenced properties).

This means that lifetime prediction for polymeric materials needs a lot of information on the ageing behavior of the material under consideration, on the artificial and outdoor exposure conditions and on the determination of relevant material properties. These requirements mean that lifetime prediction remains an art rather than a science.

For several decades, scientists had a fundamental knowledge of the weathering performance of the different types of polymeric material in use. Developments of new formulations or techniques mostly did not dramatically decrease or increase their performance. Because of a lack of confidence in results from artificial accelerated tests the different lifetimes of these new polymeric materials were, estimated by comparative artificial or/and short-time outdoor exposure tests.

During this period, the normally applied procedure of lifetime prediction consisted in simply comparing the radiant exposures from artificial tests with the expected radiant exposures in the field of application. There was no consideration of the influence e.g. of different spectral distributions of irradiance, temperatures, relative humidities and cycles of wet and dry periods. And, even now, we have no confirmation that the reciprocity law is generally valid for the different irradiance levels applied in natural and laboratory exposure tests [15.79, 80]. Only over the last two decades, the lack of confidence in results from artificial accelerated tests is decreasing and knowledge on the influence of different climatic quantities and other weather factors is continually growing.

Today, the rapid progress of developing new polymeric materials with clearly changed formulations and additives that meet the demands of new processing technologies and environmental restrictions, e.g. the

reduction of volatile organic compounds and waste disposal, does not allow sufficient durability testing by outdoor exposure. For the lifetime of their products, the producing and processing industries have to rely on data determined by accelerated exposure tests and on lifetime predictions on the basis of these data.

Therefore, there is an increasing activity of research on different methods of lifetime prediction based on reliable laboratory tests [15.25].

Key factors in further research of lifetime prediction estimates for a given polymeric material are

1. understanding actual in-service conditions and its variability,
2. understanding the influence of the variety of actions caused by outdoor exposure, and
3. confidence in results from laboratory tests at controlled exposure conditions.

15.2 Emissions from Materials

15.2.1 General

Emissions from materials influence the surrounding environment. Gaseous emissions – mainly volatile organic compounds (VOCs) – into indoor air are of special interest due to the fact that they affect indoor air quality (IAQ). VOCs are of importance because they are strongly related to the so-called sick-building syndrome (SBS). Materials are not the only source of indoor air pollution. Other important sources are every type of combustion (e.g. fire places, gas cooking), especially smoking (environmental tobacco smoke (ETS)) and the use of household chemicals (sprays, solvents e.g.). Whereas these kinds of sources can be influenced by the user (to use or not to use it) materials emissions cannot be influenced by the user to the same extent. Often the user is simply not aware that materials might have emissions.

To reduce emissions from materials, first of all knowledge is needed about

1. what is contained in the material,
2. what is emitted (quality),
3. how much is emitted (quantity),
4. duration of the emissions (time behavior, ageing).

In addition to these material parameters environmental parameters such as temperature, relative humidity, and air exchange rate influence the emissions or the resulting concentration in air.

To measure materials emissions, emission test chambers are used, which simulate environmental conditions such as those mentioned above. Air sampling and analysis is an essential part of emission testing.

15.2.2 Types of Emissions

Emissions from materials can be divided into classes of volatility and product classes depending on their field of application.

Classes of Volatility

According to [15.81,82] volatile organic compounds are divided into very volatile organic compounds (VVOCs), VOCs, semi-volatile organic compounds (SVOCs) and particulate organic matter/organic compounds associated with particulate organic matter (POM) (Table 15.6) depending on their volatility.

An important sum parameter for VOCs is the so-called total volatile organic compounds (TVOCs) value. According to ISO 16000-6, the TVOC is defined as sum of volatile organic compounds sampled on Tenax TA and eluting between and including *n*-hexane and *n*-hexadecane in a nonpolar gas-chromatography (GC) column.

Table 15.6 Classification of organic indoor pollutants according to their volatility

Description	Abbreviation	Boiling point range* (°C)
Very volatile (gaseous) organic compounds	VVOC	< 0 to 50–100
Volatile organic compounds	VOC	50–100 to 240–260
Semivolatile organic compounds	SVOC	240–260 to 380–400
Organic compounds associated with particulate matter or particulate organic matter	POM	> 380
* Polar compounds are at the higher end of the range		

Product Classes

Depending on the material and its intended field of use many chemicals are contained that might be released during the use of the material. Some examples of materials relevant to indoor use are listed here

1. lacquer, paints, coatings,
2. wood, wood-based materials,
3. furniture,
4. construction products,
5. insulating materials,
6. sealants,
7. adhesives,
8. flooring materials,
9. wall papers,
10. electronic devices,
11. printed circuit boards.

Even in the simple case of e.g. a single polymer it can still contain remaining monomers or solvents and additives from the production that can generally be emitted. Additionally special types of polymers like e.g. polycondensated resins (e.g. urea-formaldehyde resins) can be hydrolyzed and release monomers. Furthermore materials can contain a wide spectrum of additives like, e.g.

1. plasticisers,
2. biocides (e.g. from production, pot preservatives, film preservatives),
3. flame retardants,
4. photoinitiators,
5. stabilizers.

15.2.3 Influences on the Emission Behavior

The emission behavior of materials is influenced by material and environmental parameters.

Material Parameters

The following material parameters are of importance for emission behavior

1. type of material,
2. ingredients,
3. structure,
4. composition,
5. surface,
6. age.

According to [15.83] the rate of emission of organic vapors from indoor materials is controlled by three fun-

damental processes: evaporative mass transfer from the surface of the material to the overlaying air, desorption of adsorbed compounds, and diffusion within the material.

Environmental Parameters

The following environmental parameters influence emission behavior

1. temperature (T),
2. relative humidity (RH),
3. air exchange rate (n),
4. area specific ventilation rate (q),
5. air velocity.

According to [15.83] temperature affects the vapor pressure, desorption rate, and the diffusion coefficients of the organic compounds. Thus, temperature affects both the mass transfer from the surface (whether by evaporation or desorption) and the diffusion mass transfer within the material. Increases in temperature cause increases in the emissions – as can be seen in Fig. 15.14 as an example – due to all three mass-transfer processes mentioned above.

The air exchange rate is another important parameter that affects the concentration of organic compounds in indoor air. The air exchange rate is defined as the flow of outdoor air entering the indoor environment divided by the volume of the indoor space, usually expressed in units of h^{-1}. The higher the air exchange rate the greater the dilution, assuming that the outdoor air is cleaner, and the lower the concentration (see Fig. 15.15 for example).
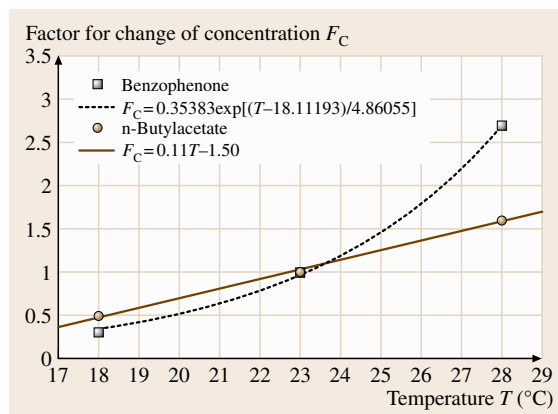

Fig. 15.14 Influence of temperature on the concentration (here the factor for the change of concentration) for a VOC and a SVOC emitted from a UV-curing acrylic lacquer applied to wood
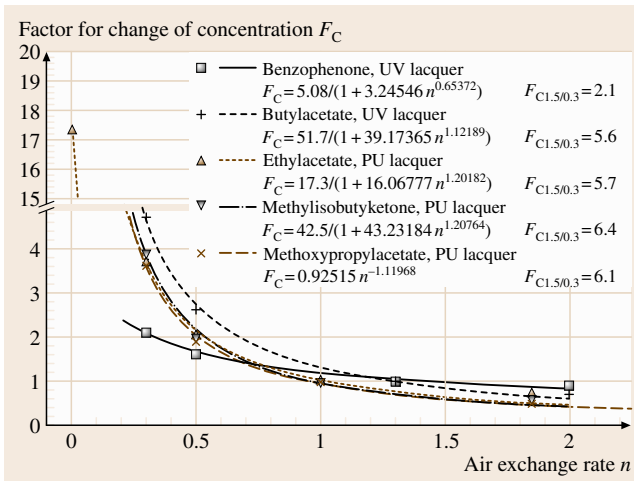
Fig. 15.15 Influence of the air exchange rate on the concentration (here the factor for the change of concentration) for some VOCs emitted from different lacquers (polyurethane (PU) lacquer, UV-curing acrylic lacquer) both applied to wood

Variation of the air exchange rate by a factor of 5 (Fig. 15.15: $F_{C1.5/0.3}$ ($n = 1.5\,\text{h}^{-1}/0.3\,\text{h}^{-1}$)) results in a change of concentration (F_C) of 5.6 to 6.4 with the exception of benzophenone. For benzophenone the concentration changes only by a factor 2.1, which is assumed to be due to adsorption effects of this SVOC.

15.2.4 Emission Test Chambers

Emission test chambers are necessary to provide defined environmental conditions for the evaluation of mater-
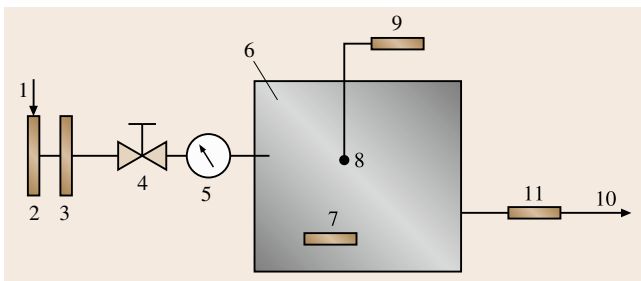

Fig. 15.16 General description of an emission test chamber (1: air inlet, 2: air filter, 3: air-conditioning unit, 4: air flow regulator, 5: air flow meter, 6: test chamber, 7: device to circulate air and control air velocity, 8: temperature, humidity, and air velocity sensors, 9: monitoring system for temperature and humidity, 10: exhaust outlet, 11: manifold for air sampling)

ials emissions. In addition to those mentioned above the following criteria have to be met

1. clean air supply,
2. emission-free or low-emission chamber materials (stainless steel or glass, low-emission sealings),
3. sufficient mixing of the chamber air,
4. tightness of the chamber,
5. low adsorption on chamber walls,
6. easy cleaning of the chamber after tests.

In Europe and meanwhile international a distinction is made between emission test chambers (EN ISO 16000-9 [15.84]) and emission test cells (EN ISO 16000-10 [15.85]). Furthermore EN ISO 16000-11 [15.86] exists, describing sampling and storing of material samples and the preparation of test specimen. It should be mentioned that these standards are made for the testing of building products, but the emission test chambers and, in the case of planar products, also the emission test cells are applicable for other kinds of materials. The chamber/cell parameters are listed in Table 15.7.

In Fig. 15.16 a general description of an emission test chamber according to EN ISO 16000-9 is shown. In Fig. 15.17 an example of an emission test cell according to EN ISO 16000-10 can be seen.

In the USA small emission test chambers are described in [15.83]. According to this standard small chambers have volumes between a few liters and $5\,\text{m}^3$. Chambers with volumes of more than $5\,\text{m}^3$ are regarded as large chambers.

Table 15.7 Specifications for emission test chambers/cells

Volume (V)	Not specified
Temperature (T)	$23 \pm 2\,^\circ\text{C}$
Relative humidity (RH)	$50 \pm 5\%\text{RH}$
Air exchange rate (n)	See q
Product loading factor (L)	See q
Area specific air flow rate ($q = n/L$)	
Flooring materials	$1.3\,\text{m}^3\,\text{m}^{-2}\,\text{h}^{-1}$
Wall materials	$0.4\,\text{m}^3\,\text{m}^{-2}\,\text{h}^{-1}$
Sealing materials	$44\,\text{m}^3\,\text{m}^{-2}\,\text{h}^{-1}$
Air velocity at the sample surface	$0.1-0.3\,\text{m s}^{-1}\,{}^{*}$
Background concentration	
Single VOC	$2\,\mu\text{g/m}^3$
TVOC	$20\,\mu\text{g/m}^3$
Minimum standard air sampling times	$72 \pm 2\,\text{h}$
(duplicate sampling)	$28 \pm 2\,\text{d}$

* only for EN ISO 16000-9,
  not mandatory for EN ISO 16000-10

For Japan small emission test chambers are described in [15.87]. Small chambers in this standard are defined to have volumes between 20 l and 1 m^3. The test temperature is $28 \pm 1\,°C$, differing from EN ISO 16000-9 and 16000-10 where it is fixed to $23 \pm 2\,°C$.

In Europe as well as in the USA additional standards for the testing of formaldehyde emissions and emissions from wood-based materials exist. These are EN 717-1 [15.88], ASTM D 6007-02 [15.89], ASTM D 6330-98 [15.90] and ASTM E 1333-10 [15.91].

In Fig. 15.18 a 1 m^3 chamber is shown loaded with an adhesive applied to glass plates for emission testing. The test specimen is brought into the center of the chamber where the air velocity is adjusted to $0.1–0.3\,m/s$. Before loading of the chamber the background concentration has been proven to be below the limits described in Table 15.7. The chamber shown [15.92] allows cleaning by thermal desorption at temperatures of up to $240–260\,°C$ in combination with a purging with clean dry air of up to four air exchanges per hour.

In Fig. 15.19 a 20 l chamber is shown also loaded with an adhesive applied onto glass plates. The conditions of temperature, relative humidity, area specific ventilation rate, air velocity, and clean air supply are the same as for the 1 m^3 chamber shown in Fig. 15.18.

In Fig. 15.20 a photograph of a FLEC is shown. The test conditions are the same as described above. Therefore even the FLEC with a volume of only 35 ml allows emission rates comparable to the emission test chambers as long as planar homogenous materials are investigated with a smooth surface where emission from small edges plays no major role.

Larger chambers with volumes of more than 1 m^3 [15.87], 5 m^3 [15.83], or 12 m^3 [15.88] might be useful if complex products like e.g. machines (e.g. printers, copiers) have to be tested for emissions. Emissions from hard-copy devices (TVOC, styrene, benzene, ozone and dust) can also be measured [15.93]. This test method has been published for measurements according to the German Blue Angel mark [15.94] and is based on the international standards for emission test chambers EN ISO 16000-9 and ISO 16000-6 for air sampling and analysis, see Sects. 15.2.5 and 15.2.6.

15.2.5 Air Sampling from Emission Test Chambers

The appropriate air sampling method depends on what has to be measured. The most common method
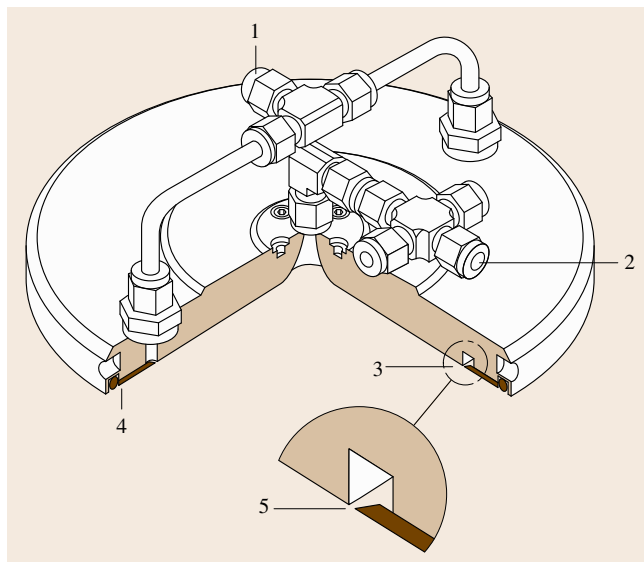

Fig. 15.17 Description of an example of an emission test cell: general description in three dimensions of the field and laboratory emission cell (1: air inlet, 2: air outlet, 3: channel, 4: sealing material, 5: slit)

Fig. 15.18 1 m^3 emission test chamber loaded for a test with a flooring adhesive on glass plates (courtesy of BAM)
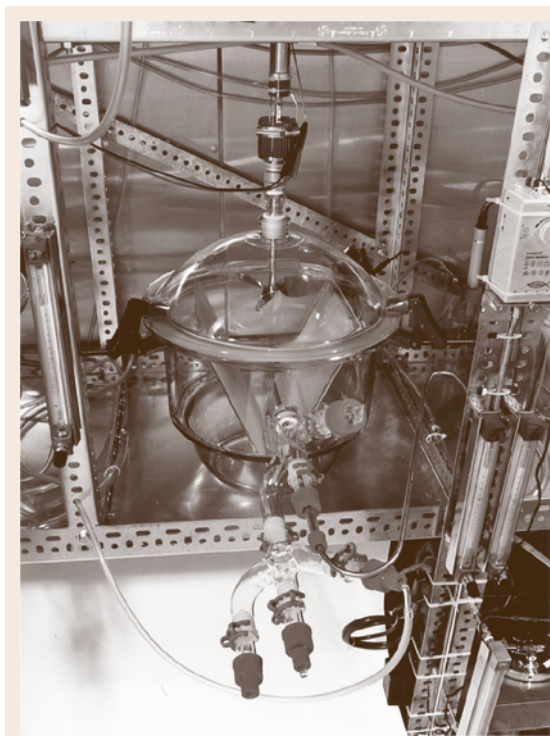
Fig. 15.19 $201 \, m^3$ emission test chamber – loaded with a flooring adhesive on glass plates (courtesy of BAM)
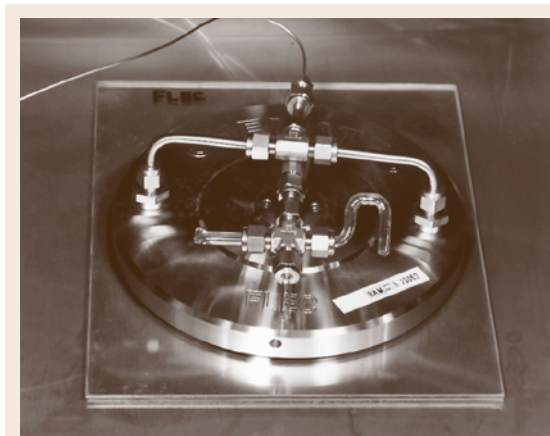

Fig. 15.20 Field and laboratory emission cell (FLEC) according to EN ISO 16000-10) (courtesy of BAM)

for VOC is sampling on Tenax (polyphenylenoxide, based on 2,6-diphenylphenol) as absorbance for enrichment according to ISO 16000-6 [15.95] and

ISO 16017 [15.96] followed by thermal desorption and analysis with gas-chromatography mass spectrometry (GC/MS, see Sect. 15.2.6). Another method being of increasing importance is sampling on 2,4-dinitrophenylhydrazine (DNPH) cartridges according to ISO 16000-3 [15.97] followed by solvent desorption (acetonitrile) and analysis by high-performance liquid chromatography (HPLC) using a diode-array detector (DAD) or UV detection (Sect. 15.2.6).

For sampling of VVOCs from air a wide spectrum of method exists that strongly depend on what has to be measured.

SVOCs can either be sampled by Tenax up to boiling points of about $360\,°C$ (n-C_{22}-alkane) [15.98] or, for higher boiling SVOCs, by special polyurethane foam (PUF) [15.99, 100] with subsequent solvent extraction. The sampling of SVOCs on PUF has been practiced successful for biocides [15.101] and flame retardants [15.102].

Table 15.8 gives an overview on sorbents for sampling of volatile organic compounds belonging to different ranges of volatility.

Figure 15.21 shows examples of sorbent tubes used for sampling of volatile organic compounds from (chamber) air.

15.2.6 Identification and Quantification of Emissions

The most common method for the identification and quantification of volatile organic compounds from air is gas chromatography with subsequent mass spectrometry (GC/MS). Using GC (Sect. 1.2) the substance mixtures are separated into the single compounds and, by MS (Sect. 2.1), the mass spectra are generated. Mass spectra can often be used successful for library searches to obtain initial information on the identity of substances. For the confirmation of identity, calibration, and quantification, authentic standards has to be used. High-performance liquid chromatography with either diode-array detectors (HPLC/DAD) or UV detectors (HPLC/UV) (Sects. 1.2 and 2.2) is used for substances for which GC is not suitable, e.g. for substances that are thermally unstable.

Figure 15.22 shows a chromatogram resulting from a chamber test of PVC flooring, air sampled with Tenax TA followed by thermal desorption and GC/MS analysis.

In Table 15.9 the substances are listed with their concentration on different days over the testing time of

Table 15.8 Guidelines for sorbent selection (after [15.103, 104])

Sample tube sorbent	Approx. analyte volatility range	Maximum, Temperature (°C)	Specific surface area (m²/g)	Example analytes
CarbotrapC CarbopackC Anasorb GCB2	(n-C_8 to n-C_{20})	> 400	12	Alkyl benzenes and aliphatics ranging in volatility from n-C_8 to n-C_{16}
Tenax TA	bp 100–400 °C (n-C_7 to n-C_{26})	350	35	Aromatics except benzene, apolar components (bp > 100 °C) and less-volatile polar components (bp > 150 °C)
TenaxGR	bp 100–450 °C (n-C_7 to n-C_{26})	350	35	Alkyl benzenes, vapor-phase PAHs and PCBs and as above for Tenax TA
Carbotrap CarbopackB Anasorb GCB1 (n-C_4)	(n-C_4/C_5 to n-C_{14})	> 400	100	Wide range of VOCs incl., ketones, alcohols, and aldehydes (bp > 75 °C) and all apolar compounds within the volatility range specified. Plus perfluorocarbon tracer gases
Chromosorb 102	bp 50–200 °C	250	350	Suits a wide range of VOCs incl. oxygenated compounds and haloforms less volatile than methylene chloride
Chromosorb 106	bp 50–200 °C	250	750	Suits a wide range of VOCs incl. hydrocarbons from n-C_5 to n-C_{12}. Also good for volatile oxygenated compounds
Porapak Q	bp 50–200 °C (n-C_5 to n-C_{12})	250	550	Suits a wide range of VOCs including oxygenated compounds
Porapak N	bp 50–150 °C (n-C_5 to n-C_8)	180	300	Specifically selected for volatile nitriles; acrylonitrile, acetonitrile and propionitrile. Also good for pyridine, volatile alcohols from EtOH, MEK, etc.
Spherocarb*	−30–150 °C (C_3 to n-C_8)	> 400	1200	Good for very volatile compounds such as VCM, ethylene oxide. CS_2 and CH_2Cl_2. Also good for volatile polars e.g. MeOH, EtOH and acetone
Carbosieve SIII* Carboxen 1000* Anasorb CMS*	−60–80 °C	400	800	Good for ultra-volatile compounds such as C_3 and C_4 hydrocarbons, volatile haloforms and freons
Zeolite Molecular Sieve 13X**	−60–80 °C	350		Used specifically for 1,3-butadiene and nitrous oxide
Coconut Charcoal* (rarely used)	−80–50 °C	> 400	> 1000	Rarely used for thermal desorption because metal content may catalyze analyte degradation. Petroleum charcoal and Anasorb 747 are used with thermal desportion in the EPA's volatile organic sampling train (VOST), methods 0030 and 0031

* These sorbents exhibit some water retention. Safe sampling volumes should be reduced by a factor of 10 if sampling a high relative humidity (> 90%)

** Significantly hydrophilic. Do not use in high-humidity atmospheres unless silicone membrane caps can be fitted for diffusive monitoring purposes. CarbotrapC, CarbopackC, CarbopackB, Carboxen and Carbosieve SIII are all trademarks of Supelco, Inc., USA; Tenax is a trademark of the Enka Resean Institute; Chromosorb is a trademark of Manville Corp.; Anasorb is a trademark of SKC, Inc.; Porapak is a trademark of Waters Corporation
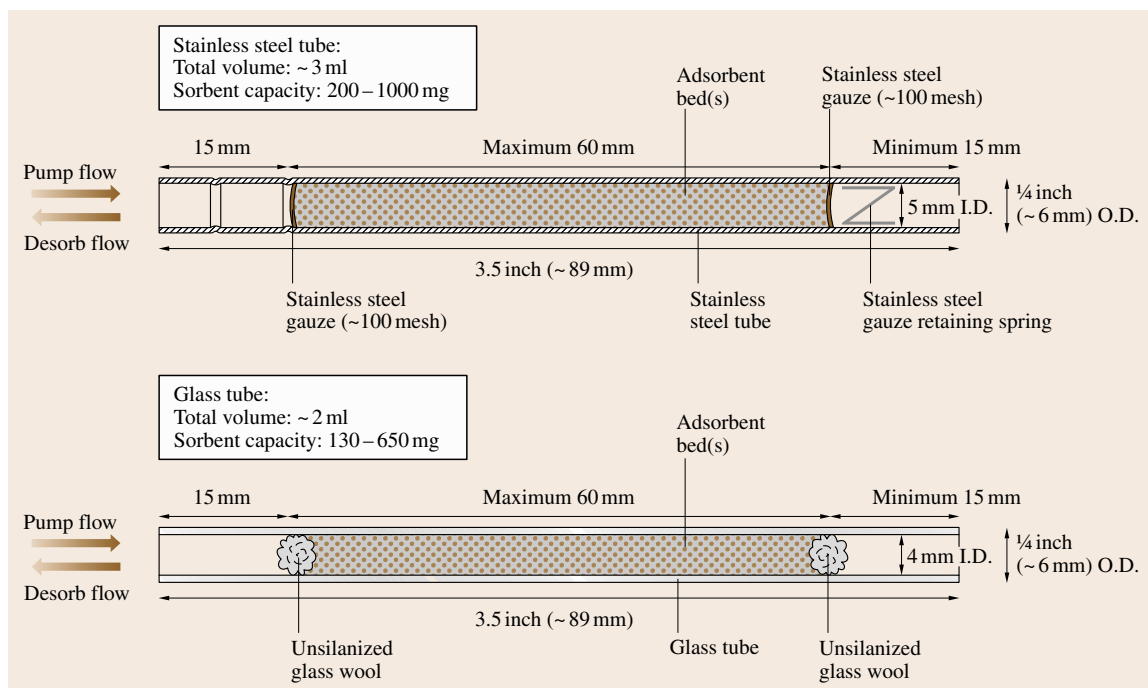
Fig. 15.21 Example of the construction of commercially available adsorbent tubes for thermal desorption

28 d. All named substances are quantified by calibration using authentic standards. The unidentified VOCs are quantified by toluene equivalents (according to ISO 16000-6 [15.95]).
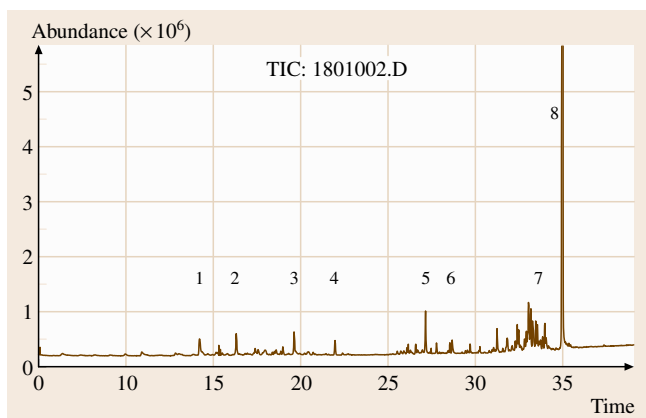

Fig. 15.22 Chromatogram from the measurement of a PVC flooring on the 28th day. 1: Methylisobutylketone (MIBK); 2: Decane; 3: Undecane; 4: Cyclodecane (internal standard); 5: Butyldiglykol; 6: *n*-methylpyrrolidone; 7: different VOCs; 8: 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB)

Calculation of Emission Rates

From the concentration of VOCs in the chamber air, emission rates (ER) or specific emission rates (SER) can be calculated. The most common for the expression of specific emission rates for materials is the area specific emission rate (SER$_a$) [15.84, 85], which is calculated from the concentration C at a certain time (e.g. 3 d (72 h) or 28 d) according to

$$\text{SER}_a = Cq = CnL^{-1} , \qquad (15.3)$$

where SER$_a$ is the are specific emission rate at a certain time [μg m^{-2} h^{-1}], C is the concentration at a certain time [μg m^{-3}], q is the area specific ventilation rate [m^3 m^{-2} h^{-1}], n is the air exchange rate [h^{-1}], L is the product loading rate [m^2 m^{-3}].

Specific emission rates can also be expressed as length, volume or unit specific emission rates. Often specific emission rates are named emission factors (EF) [15.83, 87].

15.2.7 Time Behavior and Ageing

Time behavior of material emissions can also be evaluated by means of emission test chambers. After introducing the test specimen into the chamber, 100% of

Table 15.9 List of emitted substances and their concentrations for PVC flooring for different times of testing

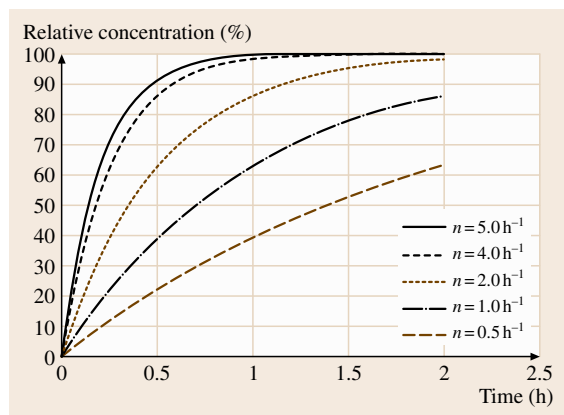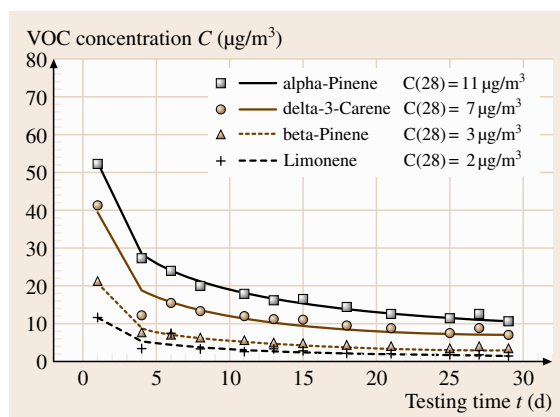| PVC	Concentration (µg/m³)						
	24 h	3rd day	7th day	10th day	14th day	21st day	28th day
MIBK (methylisobutylketone)	111	65	53	45	39	32	30
Decane	55	35	28	25	23	20	16
Undecane	44	28	22	20	18	16	13
Butyldiglycol	123	75	40	48	44	35	31
N-Methylpyrrolidon	45	30	17	20	15	13	15
VOCs ($n \approx 23$)	438	308	273	253	221	175	159
TXIB (2,2,4-trimethyl-1,3-pentandiol diisobutyrat)	1251	863	760	698	641	614	539
TVOC	2067	1404	1193	1109	1001	905	803

the equilibrium concentration is usually reached within a few hours for VOCs, depending on the air exchange rate (Fig. 15.23); the concentration is given by

$$C = SER_a(1 - e^{-nt})LV^{-1}n^{-1} , \tag{15.4}$$

where V is the chamber volume [m³].

This increase of concentration at the beginning of the emission test is mainly of interest if short-time emissions are to be investigated, for example to study the emissions from fast printing hard-copy devices (where printing time is often less than half an hour) in order to consider this for the calculation of emission rates.

If the testing time is long enough at least a trend for the variation of concentration or specific emission rates over time can be evaluated. Typically measurements in test chambers run over 28 d. VOCs during this time usually show decreasing concentrations, as can be

Fig. 15.24 Terpene emissions from a particleboard over the testing time of 29 days ($T = 23\,°C$, RH = 45%, $n = 1\,h^{-1}$, $L = 1\,m^2\,m^{-3}$, $q = 1\,m^3\,m^{-2}\,h^{-1}$)

Fig. 15.23 Theoretical percent concentration profiles for various air exchange rates
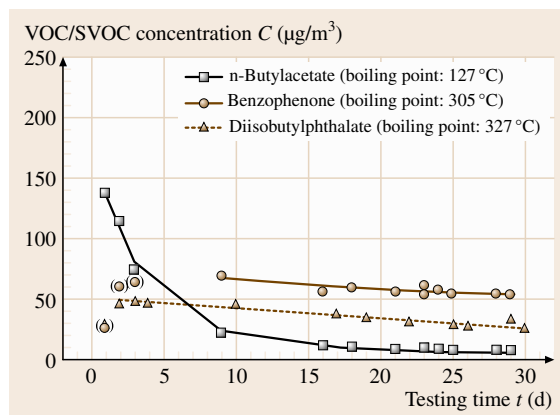
Fig. 15.25 Variation of concentration of a VOC and two SVOCs over time. Notice the increase of concentration for the SVOCs over the first few days
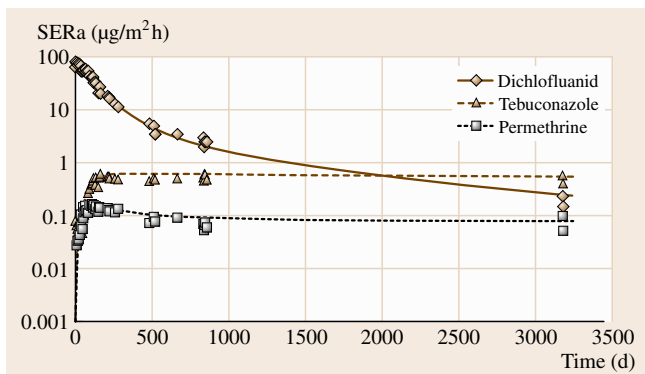
Fig. 15.26 Area specific emission rate (SER_a) for the three biocides dichlofluanid, tebuconazole and permethrine. For the increase at the beginning the SER_a has to be regarded as apparent specific emission rate due to adsorption (sink effects) on the chamber surfaces that result in reduced concentrations in air. The experiment was started in 1994 and is still running
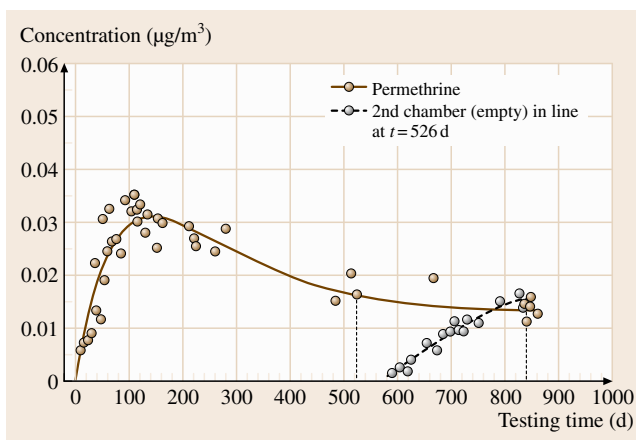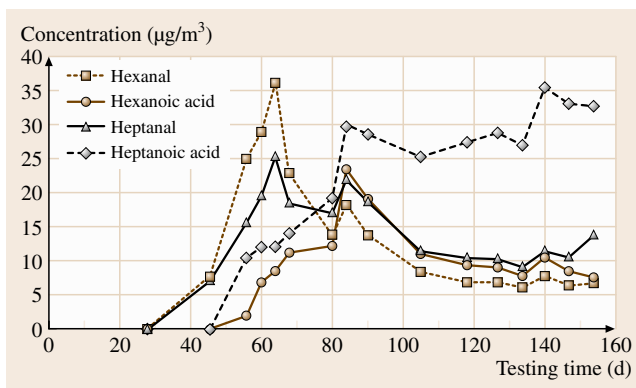

Fig. 15.27 Empty chamber connected to the test chamber: permethrine (after [15.105])

seen for example in Fig. 15.24 for terpene emissions from a particleboard. The terpene emissions result from the pine wood used for the production of the particleboard.

For SVOC emissions the decrease over time is normally not as strong as they have lower vapor pressures and therefore depletion of the boundary layer of the material takes longer. Furthermore they can show a longer increase at the beginning of the test due to adsorption effects (Fig. 15.25).

For extremely-low-volatility SVOC – often called POMs (Table 15.6) – a distinct emission behavior can generally be observed. For these substances increasing concentrations over weeks and months can be observed as shown in Fig. 15.26 for some biocides [15.101].

The time to reach the maximum concentration was about 125 d for tebuconazole and permethrine. After reaching its maximum, the concentration remained almost constant over time for nearly ten years (tebuconazole) or showed only a slight decrease (permethrine).

Generally it should be stated, that organic substances with extremely low vapor pressure show a tendency to adsorb strongly on surfaces. One result of this is that SVOC/POM are retained by the material itself and thus possibly only show slow migration to the surface of the material, slow desorption from materials surface and therefore delayed emissions. Another reason for slowly increasing concentrations is the adsorption of emitted low-volatility organic substances on inner surfaces of the emission test chamber (chamber walls): so called sink effects. Figure 15.27 illustrates this behavior for the example of a biocide (permethrin) where a second chamber was switched in line to a first chamber that was already in equilibrium [15.105]. As can be seen it took about 250 d until the second chamber was also in equilibrium. Relevant amounts of biocide where adsorbed on chamber walls that acted as sinks. This could be shown by elution of the chamber walls after the end of the test. Knowing the amount of substance transported out of the chamber by air flow together with the amount of substance adsorbed on chamber walls generally allows, even for this very-low-volatility substance, one to calculate emission rates after a shorter testing time.

Fig. 15.28 Secondary emissions from a flooring adhesive (*solid line with boxes*: hexanal, *dashed line with boxes*: hexanoic acid, *solid line with circles*: heptanal, *dashed line with circles*: heptanoic acid) ◄

15.2.8 Secondary Emissions

Secondary emissions are a special case of emissions. Measurements have shown that these emissions do not occur from the beginning of the test. They are sometimes formed during testing, as was shown for emissions from a flooring adhesive [15.103]. At the be-

ginning of the test only typical VOC emissions (mainly solvents) were detected. After more than 28 d, when a test is normally broken off, increasing concentrations of aldehydes and organic acids were already observed (Fig. 15.28). It is supposed that these are secondary products of autoxidation processes of unsaturated oils in the material or on the material's surface.

15.3 Fire Physics and Chemistry

Fire may be defined as an uncontrolled process of combustion generating heat, smoke and toxic. It is essentially of fuel available for gas phase combustion that controls the fire intensity. In fires it is the heat transfer from flames that heats liquid or solid fuels and thereby generating gaseous fumes which reacts with the oxygen in the air. This feedback process make fires an in general instable process which may either grow or go out.

Fig. 15.29 Ignition of the left side cardboard boxes occurs when the combustible volatiles are leaving the surface at a sufficient rate (courtesy of SP)

Fires cause a lot of damage to the society in form of deaths and injuries as well as economical losses. In Europe, North America, Australia and Japan the national losses of lives in fires is between 0.7 and 2.0 persons per 100 000 each year and lot more get injured. The direct economical losses are in the order of 0.1–0.3% of the GDP per year [15.106]. The cost of fire protection of buildings amounts to as much as 2.5–5% of the total cost of building and construction.

Designers and product developers strive at minimizing weight and material consumption by using materials with low densities and making products for the same purpose smaller and smaller. As will be explained below both low density and small thicknesses make materials prone to ignite and burn faster, it is important that the issue of fire properties is considered already in an early stage when developing new materials and products.

It is obvious that fire is an important aspect of the materials–environment interactions treated in this chapter, which may detrimentally influence the performance of materials, products and technical systems.

In the following – based on a brief review of the fundamentals of fire physics and chemistry – methods and techniques to characterize the fire behaviour of materials are compiled.

In addition to the methods for fire testing presented in this chapter, methods to characterize the general thermal properties of materials are compiled in Chap. 8 on thermal properties.

15.3.1 Ignition

A mixture of air and a gaseous fuel may *ignite* and burn if the concentration ratio of the fuel and the air is within the upper and lower combustion limits. For instance, the lower flammable limit of methane in air at normal temperature and pressure is 5% by volume, and the upper limit is 15% by volume. As a matter of fact, for most simple hydrocarbons, the lower and upper flammable limits in air correspond to an equivalence ra-

Table 15.10 Critical temperatures of some liquids (after *Quintiere* [15.107])

Liquid	Formula	Flash point (K)	Boiling point (K)	Autoignition point (K)
Propane	C_3H_8	169	231	723
Gasoline	Mixture	≈ 228	≈ 306	≈ 644
Methanol	CH_3OH	285	337	658
Ethanol	C_2H_5OH	286	351	636
Kerosene	$\approx C_{14}H_{30}$	≈ 322	≈ 505	≈ 533

tio of approximately 0.5 and 3, respectively. For further information about ignition reference [15.106].

Gas mixtures can be ignited either by *piloted ignition* or by *autoignition*. Piloted ignition occurs when a local source of heat or energy is introduced, while autoignition may occur momentarily for the entire volume, normally at much higher temperatures than piloted ignition.

A liquid or solid may start to burn when combustible volatiles are leaving the surface at a sufficient rate to form a combustible concentration. Piloted ignition occurs when the concentration of combustible fumes near a pilot (e.g. a small flame or a spark igniter) reaches the lower flammable limit.

The rate of evaporation for a liquid is controlled by the liquid temperature. Therefore liquids will at certain conditions reach the lower limit concentration at a given temperature called the *flash point* depending on the ease of evaporation. Table 15.10 gives the flash point temperatures, boiling temperatures and autoignition temperatures for some liquid fuels.

Time to Ignition

Most common combustible solids ignite by piloted ignition when the surface reaches a temperature of 250–450 °C. The autoignition temperature exceeds normally 500 °C, see Table 15.10 for some liquids and Table 15.11 for some plastics.

The time it takes the surface of a material (solid or liquid) to reach a critical temperature like the ignition temperature when heated depends on the dimensions and the thermal properties of the material. Two typical

Table 15.11 Ignition temperatures of some plastics, grouped by category (after *Babrauskas* [15.106])

Category of solid	Ignition temperature (°C)	
	Piloted	Auto
Thermoplastics	369 ± 73	457 ± 63
Thermosetting plastics	441 ± 100	514 ± 92
Elastomers	318 ± 42	353 ± 56
Halogenated plastics	382 ± 79	469 ± 79

cases can be identified, *thin solids* and *thermally thick solids* approximated as *semi-infinite solids*.

For *thin solids*, less than about 2 mm, the temperature is assumed uniform and the thickness is decisive for the ignition time. Then when assuming a constant total heat flux $\dot{q}''_{tot}$ (by radiation and convection) to a body surface and constant material properties, the temperature rise is proportional to the time and the heat flux over the parameter group $\rho c d$

$$T_s - T_i = \frac{\dot{q}''_{tot} t}{\rho c d} , \tag{15.5}$$

where T_s is the exposed body surface temperature, T_i the initial temperature, t time, ρ density, c specific heat capacity and d thickness. That means that time to ignition is directly proportional to the density and the thickness of a thermally thin material, i.e. the surface weight.

When a thin solid is surrounded by air at ambient temperature and heat by radiation $\dot{q}''_{tot}$ in (15.5) may be replaced by incident radiation $\dot{q}''_r$. This yield in practice just slight underestimations of time to ignition due to the disregard of cooling by convection and emitted radiation at elevate surface temperatures.

A similar expression as given by (15.5) can be derived for *thermally thick solids*, i.e. the thickness is larger than $2\sqrt{at}$, where t is time and a is thermal diffusivity, and where in turn $a = k/(c\rho)$, where k is the thermal conductivity. Then for a constant net heat flux $\dot{q}''_{tot}$ and constant thermal properties, the surface temperature rise can ideally be calculated as

$$T_s - T_i = \frac{2\dot{q}''_{tot}\sqrt{t}}{\sqrt{\pi}\sqrt{k\rho c}} . \tag{15.6}$$

The above expression indicates that the rate of surface temperature rise and thereby the time to ignition is proportional to the product of the heat conductivity k, the specific heat capacity c and the density ρ. The grouped property $\sqrt{k\rho c}$ is designated the *thermal inertia* of the material.

In this case the influence by convection and emitted radiation from the exposed surface when the tempera-

Table 15.12 Example of material thermal properties at room temperature (after *Quintiere* [15.107])

Material	Density (kg/m^3)	Conductivity (W/(m K))	Specific heat capacity (J/(kg K))	Thermal inertia (W s$^{1/2}$/(m^2 K))
Polyurethane foam	20	0.03	1400	29
Fiber insulating board	100	0.04	2000	89
Wood, pine	500	0.14	2800	440
Wood, oak	700	0.17	2800	580
Gypsum plaster	1400	0.5	840	770
Concrete	2300	1.7	900	1900
Steel (mild)	7850	46	460	12900
Copper	8930	390	390	36900

ture rises must be considered. Thus

$$\dot{q}''_{tot} = \varepsilon\left(\dot{q}''_r - \sigma T_s^4\right) + h(T_g - T_s) \,, \tag{15.7}$$

where ε is the surface emissivity and absorptivity coefficient, σ the Stefan–Boltzmann constant, h the convection heat transfer coefficient, and T_g the ambient gas temperature. Now the net heat flux $\dot{q}''_{tot}$ is not constant anymore as it depends of the surface temperature T_s. A numerical integration is therefore needed to calculate the development of T_s and thereby the time to reach the ignition temperature.

Given the incident radiation is $\dot{q}''_r$ and the ambient gas temperature equal to the initial temperature are constant, a constant $\dot{q}''_{tot}$ can, however, be obtained for calculating the time to reach ignition temperature explicitly from (15.6). Then heat transfer at the surface is approximated as

$$\dot{q}''_{tot} = \varepsilon\dot{q}''_r - \dot{q}''_{cr} \,, \tag{15.8}$$

where $\dot{q}''_{cr}$ is the critical flux at ignition i. e. the equilibrium heat flux when the surface has reached the ignition temperature T_{ig}. It may be identified from (15.6) as

$$\dot{q}''_{cr} = \varepsilon\sigma T_{ig}^4 + h(T_{ig} - T_g) \,. \tag{15.9}$$

This approximation is a constant upper limit of the magnitude of the cooling term $\dot{q}''_{cr}$ before ignition and leads to overestimates of the times to ignition. For further information on alternative approximative solutions see [15.106].

As an example the time to ignition of a surface of thick wood suddenly exposed to an incident radiation of 25 kW/m^2 is estimated. The wood is initially at room temperature and surrounded by air at the same temperature, 20 °C. The wood surface emissivity ε is assumed equal unity, convection heat transfer coefficient $h = 12$ W/m^2 K, the other thermal properties accord-

ing to Table 15.12 for pine and the ignition temperature 350 °C. Calculated surface temperature development is shown in Fig. 15.30. The full line shows the temperature when applying the heat flux according to (15.7), while the dashed line is obtained when assuming the heat flux constant with time according to (15.8) and (15.9). From Fig. 15.30 it can be noted that the ignition time is 65 s according to the full line while the approximative theory yields 100 s. The latter value can also be calculated by inserting (15.8) and (15.9) into (15.6) and solve for the time t when the surface temperature equals the ignition temperature. (A general observation by the author is that much better agreements are generally obtained by the simplified approach if the critical heat flux in (15.8) is reduced by 30%.)
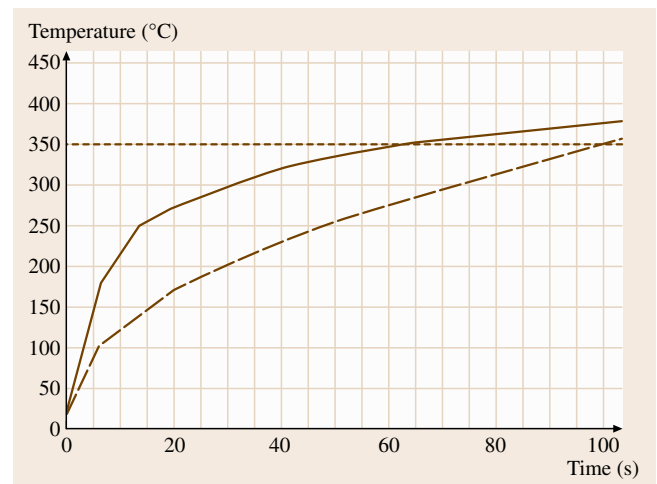

Fig. 15.30 Calculated temperature development of a wood surface exposed an incident radiation of 25 kW/m^2. The *full line* indicates the temperature development when applying (15.7) and the *dashed line* when approximating the heat according to (15.8,15.9)

Anyhow, the estimated of times to ignition as given above are very crude and based on the assumption of homogeneous materials with constant material properties, not varying with temperature or time. The formulas are, however, very useful for the intuitively understanding of which material properties govern the ease of ignition.

The thermal inertia varies over a very large range for common materials. It depends on the product of density and conductivity, and as conductivity in turn increases with increasing density. Insulating materials have low conductivities k (by definition) and low densities ρ. Therefore the influence of a change in density has a considerable influence on products fire behaviour. The specific heat capacity on the other hand depends on the chemical composition of the material and does not vary much between common materials except for wood which has a relatively high specific heat capacity. Table 15.12 shows how the thermal inertia increases considerably with density for various combustible and noncombustible materials. Note for instance that the thermal inertia of an efficient insulating material like polyurethane foam is less than a hundredth of the corresponding value of wood.

As an example a low density wood fiber board may have a density of $100 \, \text{kg/m}^3$ and a conductivity of $0.04 \, \text{W/(m K)}$, while a high density wood/fiber board have a density of $700 \, \text{kg/m}^3$ and a conductivity of $0.15 \, \text{W/(m K)}$. As such boards can be assumed to have about the same specific heat capacity, it can be calculated that the thermal inertia of the high density fiber board is more than 25 times higher of that of the low density board. The low density fiber board can therefore ideally be estimated to ignite 25 times faster than the high density fiber board when exposed to the same constant heating conditions.

Thickness and thermal inertia have also a decisive influence on *flame spread properties* of a material or product. Flame spread can be seen as a continuous ignition process and is therefore governed by the same thermal material properties as ignition. Thus the fire hazard of a material or a product can as a rule of thumb be estimated based on its density as this property governs how easily the temperature of its surface can be raised to the ignition temperature. Table 15.12 gives the thermal properties of some solid materials. These values are approximative and indicative and may vary depending on material quality as well as on measuring techniques.

Spontaneous Ignition

Self-heating leading to spontaneous ignition (commonly used interchangeable with spontaneous combustion) can take place in porous materials or in bulks of granulate solids [15.106]. It involves exothermal (heat generating) processes which raises the temperature of the material. Whether the self-heating process leads to thermal runaway and spontaneous ignition of the material or not, is a competition between heat generation and heat dissipation.

The most common heat generating process is the oxidation of organic materials in the solid phase and oxygen in the gas phase. Therefore porous materials are more susceptible to self-heating than solid materials as oxygen can diffuse through the material and reach surfaces with combustible substances in the interior of the material. A classical example of spontaneous ignition is a rag with absorbed vegetarian oil. Unsaturated fatty acids in the oil are readily oxidised, and with the large surface area and poor heat dissipation of the rag, the temperature rise is fast and leads commonly to ignition.

The problem of self-heating frequently arises in storages of e.g. agricultural products, coal, wood fuels and municipal waste. Another example is self-heating of fiberboards in storages after production [15.108]. Storages of wood chips or pellets are examples of fuels that commonly self-heat and ignite.

In storage of fuels like wood pellets, biological reactions dominate at temperatures below $100 \,^\circ\text{C}$, when the temperature has reached that level, the rate of chemical oxidation increases and the chemical reactions could further increase the temperature. The content of moisture is of importance for the self-heating process as it is necessary for the growth of biological organisms. Generally, wood fuel containing less than 20% moisture does not self-heat [15.109]. Further, vaporization and condensation of water in the bulk transport heat within the material. The moisture content of the material additionally influences the heat conduction properties. The Winds could further augment heat generating reactions by increasing the availability of oxygen.

Glowing and Smouldering Ignition

When a surface of a combustible solid is exposed to intense heat, it is changed either by melting or charring and it liberates gaseous products. The surface of a charring material may obtain very high temperatures and undergo rapid oxidation, which may be described as *glowing* ignition. When glowing in ambient air the temperature is typically in excess of $1000 \,^\circ\text{C}$. Flaming may

also occur either before or after the glowing ignition of the surface. Wood and fabrics are examples of products which may ignite first by glowing at the surface and then burn by flaming [15.106].

Smouldering can be defined as a propagating, self sustained exothermic reaction wave deriving its heat from oxidation of a solid fuel. It is a relatively slow combustion process controlled by the rate of air entering the combustion zone. The smouldering can only sustain if the material is insulating so that the combustion zone does not loose too much heat and high temperatures can be maintained. Smouldering is only common with porous or granular materials that can char. Materials which are known to smoulder under certain circumstances include [15.106]

1. wood and cellulosic products in finely divided form,
2. paper,
3. leather,
4. cotton,
5. forest duff, peat and organic soil,
6. latex foam,
7. some types of polyurethane, polyisocyanurate and phenol formaldehyde foams.

Smouldering may also occur in insulation products of mineral wool containing high levels of binders as well as in cellulose loose-fill insulations.

A smouldering fire may break out into flaming, when the combustion zone reaches for example a wood surface or when for some reason more oxygen becomes available. As smouldering fires are very slow they may last very long and may reach flaming conditions not until very long times, could in some cases be several months.

15.3.2 Combustion

A burning candle may serve as a general illustrator of burning processes. Due to heating from the flame, fuel evaporates from the wick and is transported by diffusion towards the surrounding air/oxygen. The combustion takes place at the flame, which emit light. Hot combustion products are transported upwards as they are lighter than the cool ambient air. Inside the flame envelope there are fuel vapours and no oxygen and outside it is vice versa, there is no fuel and ambient concentrations of oxygen. A candle flame is an example of a laminar diffusion flame governed by molecular diffusion.

Flames may be categorized as diffusion flames or premixed flames. In *diffusion flames* fuel gas and oxygen are transported into a reaction zone and mixed due to concentration differences. In *laminar flames* the diffusion is by molecular diffusion. In flames larger than about 30 cm the laminar flow breaks up into eddies and we get a *turbulent diffusion flame*. Although laminar flames may be important in the ignition phase of a fire, the *turbulent* diffusion flames are the most significant in real fires.

Burning Rate

Burning rate is defined as the mass loss of solid or liquid fuel consumed by combustion per unit time. A general formula the mass burning rate may be written as

$$\dot{m}'' = \frac{\dot{q}}{L} \, ,$$

where $\dot{q}$ is the net heat flux to the fuel surface and L the heat of gasification. The latter is a material property. Typical values of L are given in Table 15.13.

When burning the fuel surface is heated by radiation and convection by nearby flames and hot gases. Heating by *radiation* may also come from other sources like remote flames, layers of combustion gases or hot surfaces. The temperature of the surface of thermoplastics and liquids will in principle be at the boiling point. For charring materials like wood and thermosetting plastics an insulating char layer will form, which will hamper the heat flux to the surface and thereby reduce the burning rate.

The *heat release rate* (HRR) or energy release is the most important quantity for characterizing a fire. It rep-

Table 15.13 Values of heat of gasification and effective heat of combustion (after *Quintiere* [15.107])

Fuel	L (MJ/kg)	ΔH_c (MJ/kg)
Liquids		
Gasoline	0.33	43.7
Heptane	0.50	43.2
Kerosene	0.67	43.2
Ethanol	1.00	26.8
Methanol	1.23	19.8
Thermoplastics		
Polyethylene	1.8−3.6	43.3
Polypropylene	2.0−3.1	43.3
Polymethyl metha-crylate (PMMA)	1.6−2.8	24.9
Nylon 6/6	2.4−3.8	29.6
Polystyrene foam	1.3−1.9	39.8
Char formers		
Polyvinylchloride (PVC)	1.7−2.5	16.4
Woods	4.0−6.5	13.0−15.0

Table 15.14 Yields of carbon monoxide CO Y_{CO} and mass optical density D_m depending on ventilation (after *Quintiere* [15.107])

Fuel	Overventilated or fuel lean conditions Y_{CO} (kg/kg)	D_m (m²/kg)	Underventilated or fuel rich conditions Y_{CO} (kg/kg)
Propane	0.005	160	0.23
Heptane	0.01	190	NA
Wood	0.004	37	0.14
Polymethyl methacrylate (PMMA)	0.01	109	0.19
Polystyrene	0.06	340	NA
Polyurethane flexible foam	0.03	330	NA
Polyvinylchloride (PVC)	0.06	400	0.36

resents the size of the fire and relates directly to flame height and production rates of combustion products like smoke and toxic gas species.

The heat release rate $\dot{q}$ is the product of the burning rate $\dot{m}''$ and ΔH_c

$$\dot{q} = \dot{m}'' A \Delta H_c$$

where A is the fuel area involved. The effective heat of combustion is a material property (Table 15.13).

Combustion Products

The nature of the combustion products developed in a fire depends on the fuel as well as on the entire fire process. The chemical reactions occurring in the decomposition of the fuel and in the reaction with oxygen depend on temperature, gas flow conditions, ratio between fuel and air available for the combustion process etc. If more air is available than needed for a complete burning process the condition is assumed to be over ventilated or process fuel lean. For less air, the process is termed underventilated or fuel rich. If the fuel to air ratio perfectly match the burning process is *stoichiometric*. A parameter that quantitatively represents over- and underventilation in fires is the equivalence ratio ϕ defined as

$$\Phi = \frac{(\text{mass of fuel/mass of air})}{(\text{mass of fuel/mass of air})_{\text{stoich}}} .$$

Thus for $\Phi < 1$ the fire is fuel lean and for $\Phi > 1$ fuel rich.

In a similar way as the heat of combustion gives the energy release, *yields* give the mass production rate of combustion product species per unit mass of fuel. As an example the rate of CO mass produced $\dot{m}_{CO}$ can be calculated as

$$\dot{m}_{CO} = \dot{m} Y_{CO}$$

where $\dot{m}$ is the rate of burning and Y_{CO} the yield of CO. The yields of various species are reasonably constant as the fire conditions are well ventilated $\phi < 1$. Under fuel rich conditions $\phi > 1$, however, the yields changes and the production rates increases for many toxic species. Yields of carbon monoxide are given in Table 15.14.

Light is attenuated by *smoke* mainly due to soot particles. Smoke has in many cases a decisive influence on the ability to escape a fire. Therefore the propensity of a material to release smoke is an essential fire property of a material. The reduced intensity of light I can be measured with a lamp and photocell at a distance l away and be expressed as

$$I = I_0 e^{-\kappa l} ,$$

where I_0 is the original intensity. The parameter κ is the extinction coefficient with the dimension one over unit length (m^{-1}). For a given mass of fuel burnt material m in a closed volume V the extinction coefficient κ may be obtained as

$$\kappa = \frac{m D_m}{V} ,$$

where D_m is the mass optical density with the dimensions mass over area (kg/m²), which is a material property for overventilated conditions. Values for some common products are given in Table 15.14.

Toxic Products

Organic fuels like wood and polymers contain mainly carbon and hydrogen. Thus when burning with enough oxygen available (fuel lean conditions) the combustion process may be completed and mainly carbon dioxide and water are generated. However, under fuel rich conditions or when the combustion process is interrupted due to cooling (quenching), the combustion process is incomplete and several chemical species are generated

which may be toxic. The most important is *carbon monoxide* which is the cause of most fire casualties. Products containing *nitrogen* like polyurethane may generate toxics substances like hydrocyanic acid HCN and *isocyanates* which have a very high toxic potency.

Soot particles may also constitute a toxicological threat as they can transport toxic species from fires adhered to their surfaces deep into the lungs.

Corrosive Products

Some products like polyvinylchloride PVC generate acid gases like HCl when burning, which is irritating for the eyes and air passages although not necessarily fatal during inhalation. This may hamper the evacuation of a building on fire. In addition HCl dissolves in water droplets and forms hydrochloric acid, which is highly corrosive and may deposit on metal surfaces and cause damages. Such corrosive damages may show up long after a fire and cause a great threat to electronic equipment which in many cases must be discarded after a fire although not being directly exposed flames or hot gases and seemingly being undamaged.
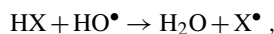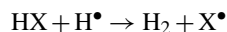
Flame Retardants

There are numerous chemical compounds used to inhibit the combustion process in materials, mainly plastics. Flame retardants can function by intervening in the combustion process chemically or physically, or through a combination of both. Common for all flame retardants is that they interfere early in the combustion process during the heating phase or the ignition phase.

Physically a flame retardant additive can act as a barrier by forming a layer of char when exposed to heat. This layer then protects the underlying material from heat and thereby from degradation and the ensuing generation of combustible fumes. Further, these flame retardants remove the direct connection between the oxygen in air and the fuel [15.110]. Flame retardants can also act by cooling. In such cases the additive degrades endothermally, thereby cooling and possibly diluting the gas mixture of the combustion process, for example through the production of water vapour. In certain instances additives can be used that act only by diluting the material with inert substances such as fillers. This will typically reduce the heat release from a certain weight of a material but have little effect on the ignitibility of the material per se.

Chemically flame retardants can act by accelerating the initial breakdown of the material, causing the material to withdraw from or to flow away from the ignition source or by promoting the generation of a char

layer. Other flame retardants may act in the gas phase through removal of free radicals that are the motor in the exothermic combustion process. The process is shown by the formula below

$$HX + H^\bullet \rightarrow H_2 + X^\bullet$$
$$HX + HO^\bullet \rightarrow H_2O + X^\bullet \,,$$

where X represents a halogen.

The main families of flame retardants are *halogenated* (i.e., containing chlorine or bromine), *phosphorous* based, *nitrogen* based, inorganics and others (including antimony trioxide and nanocomposites). Many of these systems work either in isolation or together with some systems exhibiting synergistic effects when used in combination.

Brominated flame retardants have the highest market share in terms of turnover while *aluminum hydroxide* has the highest market share by weight. A global growth of approximately 3% has been projected by the flame retardants industry in the near future with inorganic flame retardants (e.g. aluminum hydroxide) having the highest projected growth rate.

Flame retardants have received broad application in correlation with the ubiquitous use of plastics in our society. While certain plastics have unacceptable ignition and flame spread properties, they also exhibit highly desirable mechanical properties, i.e., their ability to be formed into a myriad of shapes and applications. Thus, the safe application of plastics has at least partially been dependent on the use of flame retardant additives to modify undesirable ignition and flame spread properties.

In recent years *environmental concerns* about many of these additives has prompted questions about the suitability of their broad use. Legislation is under way in Europe and elsewhere to control the use of these chemicals. Research into quantifiable tools to determine the true environmental impact of the use of flame retardants to obtain a high level of fire safety have, however, clearly identified the need to consider such issues holistically [15.111].

15.3.3 Fire Temperatures

Temperatures in natural fires depend on actual combustion conditions such as fuel/air ratio and heat losses to the environment mainly by radiation. Thus the maximum temperature of turbulent diffusion flames of free-burning fires is in the order of $800-1200\,°C$. Fires in enclosures with limited openings may at the most reach temperatures in the order of $1200\,°C$.

Mechanically ventilated fires may under certain very favourable conditions for combustion develop extremely high temperatures. Thus fires in tunnels may reach temperatures of nearly 1400 °C with ordinary fuels of cellulosic materials. Temperatures of that order of magnitude were measured in several tests carried out in a tunnel in Norway 2003 where fires in trailers loaded with wood pallets and furniture were simulated. Such temperature levels expose the surrounding tunnel walls to devastating thermal loads causing concrete linings to spall and fall off in pieces. Therefore tunnels linings must be designed to resist much higher temperatures than other building structures.

Room Fires

The various stages of a fire in a room or compartment with limited openings are shown in Fig. 15.31. Initially the fire is not affected by the surrounding structures. In this *growth stage*, which may last from a few minutes to several hours, the fire intensity is *fuel controlled*. As the fire intensity increases the temperature rises and more and more combustible fumes are released. At a certain stage the fire may start to grow rapidly and *flashover*. After that in the *post-flashover* stage the fire consumes all available oxygen inside the compartment. It is then a *ventilation controlled* or *fully developed* fire. The combustion rate at this stage depends on the amount of oxygen or air that can enter the fire compartment, i. e. it depends on the size and shape of the compartment openings. At this stage the fire generates a lot of heat, smoke and toxic gases, and the temperature of the combustion gases is at least 600 °C and rises as the surrounding structures, i. e. walls, floors and ceilings heats up. Excess combustible fumes will at this stage emerge
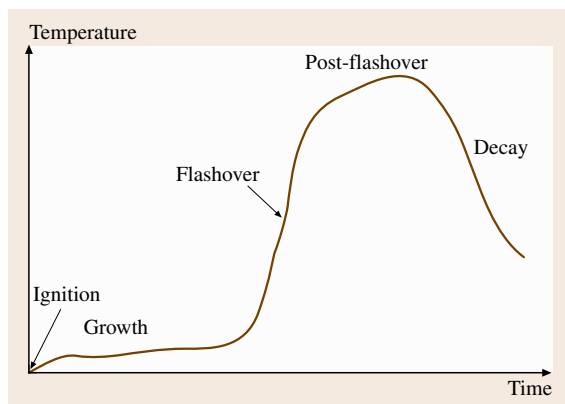

Fig. 15.31 General description of the various stages of a room fire (courtesy of SP)
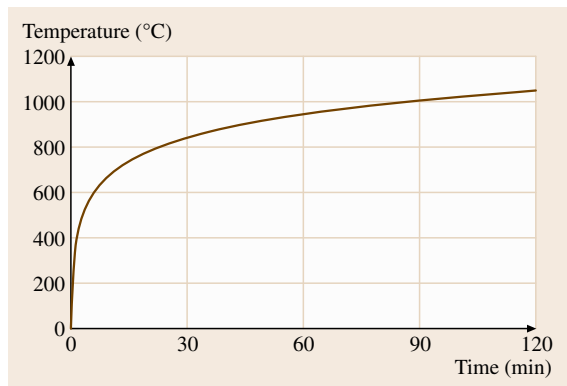

Fig. 15.32 The standard time–temperature curve according to EN 1363 or ISO 834

outside the compartment openings and burn as flames shooting out from the openings. *Flashover* represents a crucial event in the development of a fire as it goes from being a local fire in one room or compartment to a much more severe fire having the potential of rapidly spreading heat and smoke throughout a building.

Significant building components must be designed to resist a fully developed fire. Such a fire is then usually simulated by the so called standard fire curve as shown in Fig. 15.32. This time–temperature curve is meant to simulate a typical fire at the post-flashover stage.

Compartments fire developments can be numerically modelled in three ways [15.112]. The simplest are the *one-zone models* where the entire compartment gas volume is assumed to be at uniform temperature. Mass flow in and out of the compartment is driven by buoyancy. Hot fire gases are lighter than the ambient air and flow out at the top of the openings and are replaced by cool fresh air further down. The fire temperature development will depend on the thermal inertia of the surrounding structure and on the size and height of the openings. Lower thermal inertia (in principle low density) and large openings implies faster fire growth higher temperatures. One-zone models are suited only for fully developed fires. In *two-zone models* the fire compartment is divided into an upper hot zone with fire gases and a lower zone with air at ambient temperature (Fig. 15.33) models are suited for fires before reaching flashover. More advanced are the so called CFD (computational fluid dynamics) models where the compartment is divided to a large number of volume elements. Then arbitrary fire conditions can be analysed in terms of temperature as well as concentrations of smoke and (toxic) gas species. CFD models are very
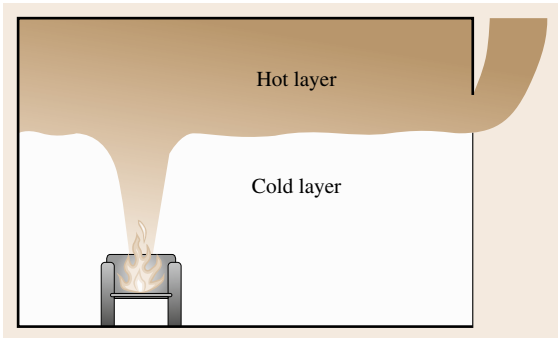
Fig. 15.33 Two-zone model of a room fire with an upper hot layer and a lower layer at ambient temperature (courtesy of SP)

powerful but require substantial computer capacities and detailed material property data.

15.3.4 Materials Subject to Fire

Structural Materials

The temperature in structures exposed to fully developed fires with gas temperatures reaching 800–1200 °C will gradually increase and eventually the structures may loose their load-bearing capacity as well as their ability to confine the fire to a limited space. In building codes fire resistance requirements are usually expressed in terms of time of a structure to resist a nominal or standard fire defined for example in the international standard ISO 834 or the corresponding European standard EN 1363-1 (Fig. 15.32). In USA the corresponding standard for determining fire resistance of building components is ASTM E-119.

Steel starts to lose both strength and stiffness at about 400 and above 600 °C more than half the strength is lost [15.113]. Therefore structural steel elements must in most cases be fire insulated by sprayed on compounds, boards, mineral wool or intumescent paint to keep sufficient load-bearing capacity when exposed to fire. An example of a steel structure failure due to fire was the collapse of two World Trade Center towers on September 11, 2001 after each of them had been hit by a big passenger airplane. A tremendous impact on the buildings but they did not collapse until after about half an hour. The jet fuel had started intense fires and when the strength and stiffness of the steel structures had been eroded due high temperatures the structures failed.

Concrete also looses strength and stiffness at high temperature [15.114]. This is, however, generally not a problem as concrete has a high density and specific heat capacity as well as a low thermal conductivity. Therefore temperature rises slowly in concrete structures and even the steel reinforcement bars are in general well protected. More problematic is the tendency of concrete to spall when exposed to high temperatures. In particularly high strength concrete qualities are prone to spall. Spalling is not least a problem when designing road and railway tunnels where fire temperatures may be extremely high and where a collapse of a tunnel lining may have devastating consequences.

Wood looses both strength and stiffness as well at elevated temperature. It burns and chars gradually at a rate of about 0.5 mm/min when exposed to fire conditions. The char layer protects the wood behind from being directly exposed to fire conditions and thereby quickly heated and losing its load-bearing capacity. Timber structures therefore resist fire rather very well and can in many cases be used unprotected, see e.g. Eurocode 5 [15.115]. In many cases structural timber members like wall studs are protected from direct exposure by fire boards of for example gypsum and can therefore resist fire for very long periods of time.

Fig. 15.34 The jet fuel started intense fires that caused the World Trade Center towers to collapse on September 11, 2001

Polymers and Composite Materials

Thermoplastics and thermosetting materials decompose differently when exposed to heat. Thermoplastics can soften without irreversible changes of the material, while thermosetting materials are infusible and can not undergo any simple phase changes. They do not have a fluid state.

Many thermoplastics and thermosetting materials form chars when decomposed by heat. This char is as for wood in general a good insulator and can protect the underlying virgin material from heat and slow down the decomposition process.

The polymers possess different hazards in fires depending on their physical constitution and chemical composition. Foamed plastics and thin plastics ignite more easily and burn more vigorously than solid plastics. Below some characteristics are given for a few commercially important polymers. The thermal stability of *polyolefins* like polyethylene and polypropylene depends on branching of the molecule chains, with linear polymers most stable and polymers with branching less stable. *Polyvinylchloride (PVC)* has in general good fire properties as the chloride works as a flame retardant agent. However, the hydrogen chloride HCl, which is generated while burning, is corrosive and irritating and toxic and can impede the evacuation from a fire. *Polyurethanes (PU)* contain nitrogen and forms very toxic products like hydrogen cyanide and isocyanates. PVC and PU do also generate very dens smoke.

Composite materials consisting of a polymer and suitable reinforcing fibers (typically, glass, carbon or aramide material), also called fiber reinforced plastics (FRP), have become increasingly used in many areas of construction, such as airplanes, helicopters and high-speed crafts, due to the high strength/weight ratio. These materials are also chemically very resistant and do not corrode or rust. They are, however, combustible and as they are often meant to replace noncombustible materials, (steel, concrete) they could introduce new fire hazards. Another concern is that inhalable fibers might be generated from FPR-materials when burning. These fibers may also penetrate the skin causing irritation and inflamation, and carry toxic substances into the body. This could be a particular hazard when composite materials are mechanically destructed, e.g. in an air plane crash, when large amounts of fibers are released and become airborne.

15.3.5 Fire Testing and Fire Regulations

A lot of products to be put on the market need some kind of documentation, approval or certification, on their fire properties. These documents are usually based on fire tests performed according to various standards. Several organizations issue such standards which describes in detail how the tests shall be carried out. Nationally the most well known standards organizations issuing fire test standards are BSI in UK, DIN in Germany, and ASTM and NFPA in USA. Internationally both the European Committee for Standardization CEN and the International Organization for Standards ISO are very active in the field of fire safety.

There are mainly three categories of fire tests, reaction-to-fire, fire resistance and fire suppression tests. The *reaction-to-fire tests* evaluate materials and products properties in the early stage of a fire. They measure for example ignitibility and flame spread properties. Tests for measuring generations of smoke and toxic gases are often also associated with this cate-

Fig. 15.35 Fire-resistance testing of a glazed partition (courtesy of SP)

gory of tests. *Fire resistance tests* measure how long structural and separating building components can resist a fully developed fire from spreading from one compartment to another. A fire is than simulated in a fire resistance test furnaces (Fig. 15.35), where the temperature develops according to a standardized time-temperature curve as specified in e.g. EN 1363-1, ISO 834 or ASTM E-119. The specimen is then exposed to the simulated fire conditions. The temperature is measured on the other unexposed side and must during the test not rise so much that ignition can occur there. Neither must any flames come out on the unexposed side. Load-bearing elements must be able to carry their design load during the entire test period. *Fire suppression tests* are carried out on extinguishing media, e.g. dry powders and fire extinguishing foams, and on extinguishing equipment like sprinklers, portable extinguishers etc. The latter are tested in full scale and classified according the type of fires, cellulosic fuels, gasoline or electric equipment, and size of fires they can extinguish.

Buildings

A new testing and classification system for building materials and products has been developed within the European Committee for Standardization CEN and is gradually being introduced in the national regulations of the EU member states. Many building materials and products need to be tested as a basis for classification

and CE-marking. This is a harmonized way of declaring certain product properties regulated by EU member states.

For *reaction-to-fire* the so called Euroclasses A–F with several subclasses have been defined for construction products [15.116]. F means that no fire criterion has been declared. The classes A1 and A2 mean the products are denoted as more or less noncombustible. Example of class A1 products are totally inert materials like steel or concrete. A2 products contain limited amounts of combustibles like mineral wool insulations where the binder is combustible and may burn. Methods for carrying out the appropriate test are defined in the standards EN ISO 1182 Noncombustibility and EN ISO 1716 Calorific potential. For class A2 tests in the SBI (single burning item) apparatus according to EN 13823 (Fig. 15.36), are required as well.

To reach class B–D tests have to be done in the SBI apparatus and in the small flame test rig according to EN ISO11925-2. Typical materials in class B are gypsum boards covered with carton. In class D you find for example solid wood panels.

The level of fire safety requirements in various types of buildings and occupancies are specified in national building codes. The level of safety depends on the character of the building in terms of height, occupants and use etc. The most rigorous requirements are in large and tall buildings and in public buildings where people stay overnight, e.g. hotels and hospitals. Surface linings
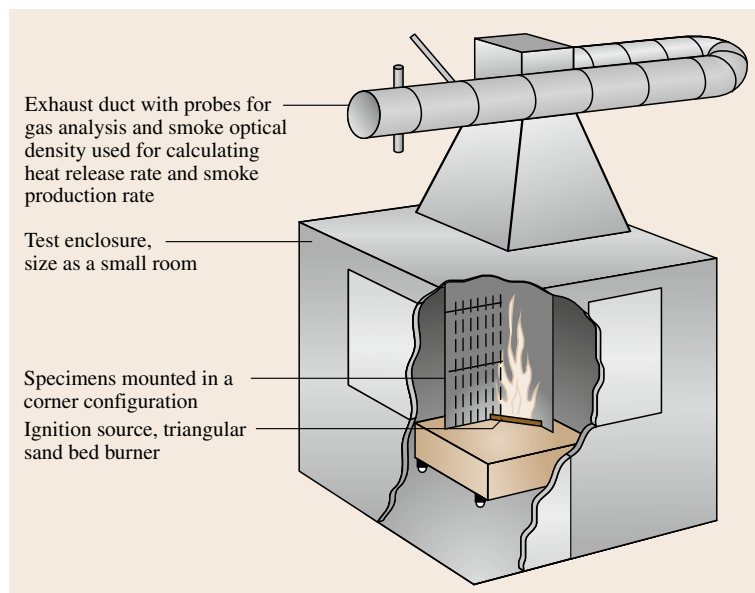
Exhaust duct with probes for gas analysis and smoke optical density used for calculating heat release rate and smoke production rate

Test enclosure, size as a small room

Specimens mounted in a corner configuration

Ignition source, triangular sand bed burner

Fig. 15.36 In the SBI method (EN 13823) the 1500 mm high test specimens are placed in a corner (courtesy of SP)
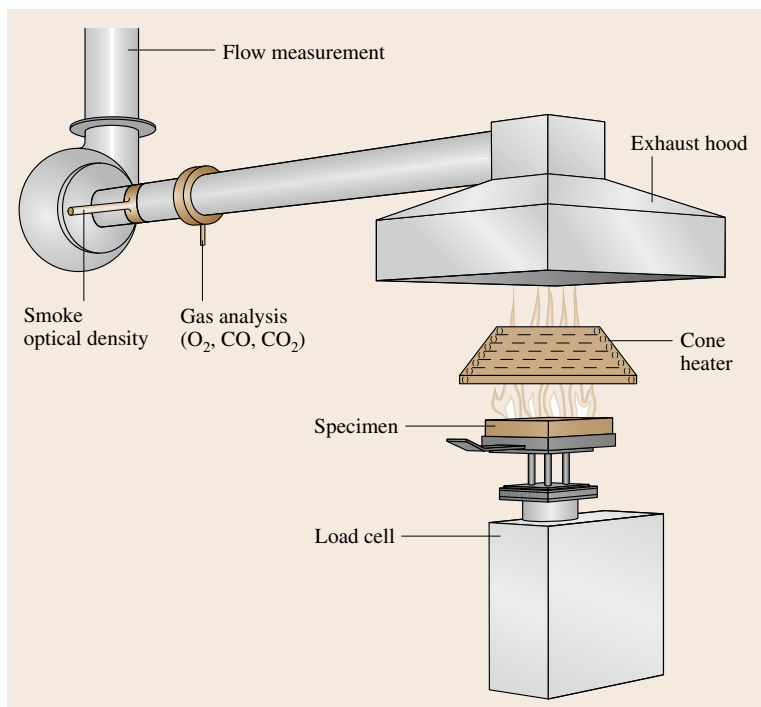
Fig. 15.37 The cone calorimeter measures heat release per unit area when a specimen is exposed to a given heat irradiance (courtesy of SP)

Flow measurement

Exhaust hood

Smoke optical density

Gas analysis (O$_2$, CO, CO$_2$)

Cone heater

Specimen

Load cell

in for example escape routes must generally have very good fire properties, of class B or better.

Building elements may fail a fire resistance test as described above either by integrity, insulation or loss of load-bearing capacity. An integrity failure means that flames penetrate through an element meant to separate two rooms or fire cells in a building. Correspondingly an insulation failure means in short that the temperature rise on the unexposed side of a separating element exceeds 140 °C. Building elements are classified in terms of their fire resistance time, i. e. the time elapsed before failure in a fire resistance test. National building codes then specifies required fire resistance times of building elements and components depending on the level of risk of a failure, mostly in the range of 30–120 min. The former may refer to apartment doors in domestic dwellings and the latter to structural elements in high rise buildings.

In USA the so called Steiner tunnel test ASTM E 84 is the major test method used for determining surface burning characteristics of wall lining materials.

Internationally ISO has published similar standards as CEN for testing fire properties of building products. Of special interest for material developers is the Cone Calorimeter ISO 5660-1, as shown in Fig. 15.37, for measuring heat release rates per unit area as a func-

tion of time of products when exposed to specified levels of heat irradiance. The results of these tests can among other things be used in fire safety engineering to calculate the heat release rates in full scale scenarios [15.117].

Transportation

Combustible plastics are increasingly used in transportation vehicles. They have in comparison with metallic materials several advantages. However, they all burn more or less. Therefore several test methods have been developed in the various sectors of transportation to evaluate their burning behaviour. The transportation industry is by nature very international, as vehicles are often marketed worldwide and used in several countries. Rules and regulation as well as test methods are therefore increasingly international. In some cases test methods are published by international standards bodies. In other areas the rules of US authorities have become so dominating worldwide that they in practice can be considered as international. Below some fire test methods used internationally in various sectors are presented briefly.

For *motor vehicles* the US Federal Motor Vehicle Safety Standards (FMVSS) has great influence on the industry worldwide. The most significant standard is the

small scale flame spread test FMVSS 302 [15.118] for motor vehicle interior components (Fig. 15.38).

The UIC (Union Internationale des Chemins de Fer) has established a code covering regulations and recommendations for *rail vehicles* or *trains*. The fire tests in this code are mainly simple ignition tests. The code has, however, only partly been adopted in some European countries. Thus there has been work going on within CEN and CENELEC since 1991 to form a harmonised standard named EN 45545 Railway Applications – Fire protection of railway vehicles. The new standard will use modern fire test methods like the cone calorimeter (ISO 5660) and the smoke density chamber (ISO 5659). It will also require smoke toxicity assessment of interior materials in trains.

There are numerous national test standards for trains. In Germany DIN 5510 the vertical Brandschacht test (DIN 54 837) is the main method regulating ignition, fire spread, smoke and flaming droplets. France uses NFF 16-101 which also includes toxicity assessment of materials. In Great Britain the national standard is BS 6853 which divides train vehicles into operation categories with varying fire requirements, the main test being a radiant panel test for flame spread. The British standard also considers design and demands on fire detection, suppression and alarm systems.

For *aircrafts* most countries have adopted wholly or in relevant parts the Federal Aviation Regulations (FAR) [15.120] of the US Federal Aviation Administration (FAA). The methods used to fire test the materials and components of the holds of transport airplanes are for example described in FAR part 25. The requirements for military aircrafts are partly similar.

For most parts used in the interior of aircrafts FAR part 25 requires that material and components shall pass so called Bunsen burner-type tests where the specimen is mounted in different angles depending of end use. Figure 15.39 shows the test where the specimen is mounted horizontally used for demonstrating that materials are *self-extinguishing*. Other fire tests are specified for components like seat cushions, cargo compartment liners, etc. Some tests not used elsewhere are specified for measuring certain fire properties. Thus for example the so called OSU apparatus is specified for measuring heat release, and a special *fireproof* and *fire-resistance* test is described in FAR part 23 for materials and parts used to confine fires in designated fire zones.

Safety of international *trading ships* is regulated by the International Convention for the Safety of Life at Sea (SOLAS) since 1974. SOLAS includes a set of fire safety regulations in its chapter II-2. This chap-
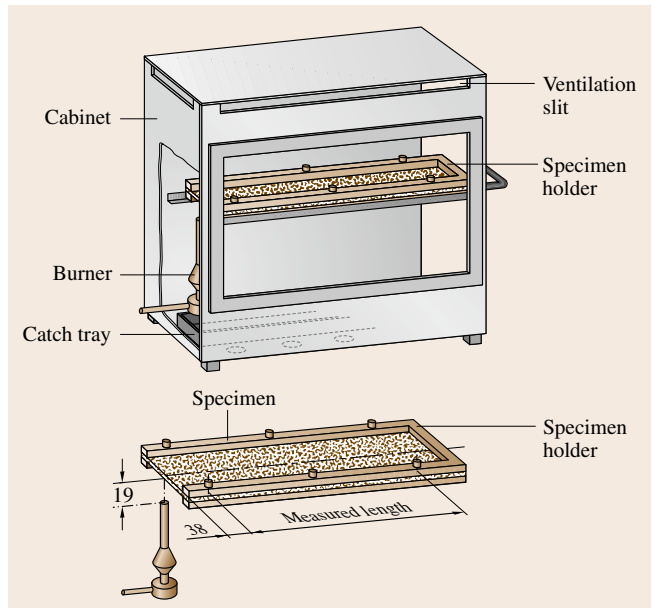

Fig. 15.38 US Federal Motor Vehicle Safety Standard FMVSS 302 rate of flame spread test for motor vehicle interior components (after [15.119])

ter is reviewed by the Fire Protection Sub-Committee (FP) of the International Maritime Organization (IMO). In 1996, IMO FP developed the Fire Test procedures Code (FTP Code) which contains the test procedures for fire safe constructions and materials used on board ships.

Electrical Engineering

Combustible plastics are used extensively in electrical engineering because of their durability, corrosion resistance, strength and not least electrical insulation properties. However, plastics can burn and as any energized circuit inherently is a fire hazard special precautions must be taken with these products. The International Electrotechnical Commission (IEC) and the European Electrotechnical Standardization Commission CENELEC prepare and publish fire test standards for electro technical products and cables. Thus a comprehensive series of fire tests have been published in the standard IEC 60695 for characterizing various fire properties like ignitability, flammability, smoke obscuration, toxic potency, and resistance to abnormal heat. In Europe CEN is underway to make available a similar classification system for cables as for building materials. It will be based on the preliminary test standard prEN 50399-2.
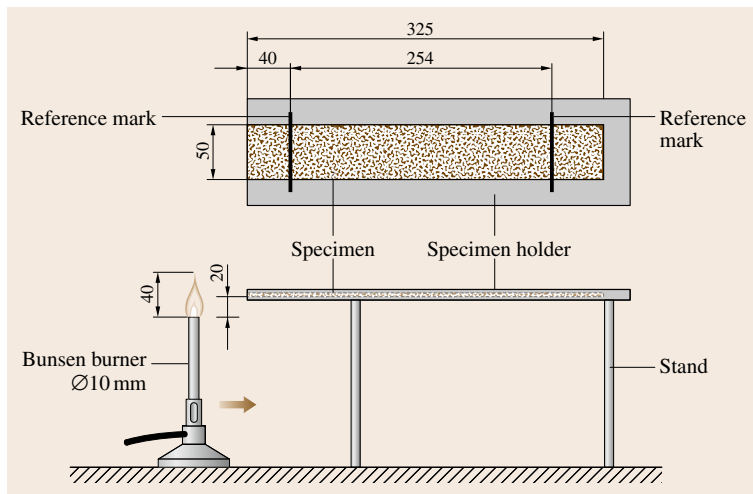
Fig. 15.39 FAR part 25 testing in horizontal position (after *Troitzsch* [15.119])

Furniture

Furniture, in particular upholstered furniture of polymer foams like foam rubber, can burn intensively and is therefore a potential fire hazard unless properly designed. Most countries have strict building regulations but the fire safety requirements on the building contents like furniture is in general very modest although a survey in Europe [15.119, 121] shows that fires in furniture cause nearly 50% of all fatal fires in private dwellings.

Fig. 15.40 Furniture calorimeter for measuring heat release at full scale of pieces of furniture (courtesy of SP)

There are several test methods published by various standardization bodies. The European Standard Organization CEN has published four ignition test standards for upholstered furniture and for mattresses. EN 1021-1 and EN 1021-2 are cigarette and small-flame tests for upholstered seatings, and EN 597-1 and EN 597-2 are cigarette and small-flame tests for matresses [15.119].

Furniture is a complicated product comprising many different materials and assemblies. Fire may develop in cavities and beneath the covering layer etc. or as pool fires underneath a piece of furniture. Therefore any small scale test of individual materials is not always suitable for assessing the fire hazard of composites of cover and filling. To estimate the fire behaviour of these in more realistic fire situation, full scale test data from e.g. the furniture calorimeter as described in NT FIRE 032 is needed (Fig. 15.40). An internationally wide spread method is the full-scale room test according to Technical Bulletin 133 of the State of California [15.122]. This method is in part intended for furniture in high-risk and public occupancies like prisons, health care facilities, public auditoriums and hotels.

The Cone Calorimeter ISO 5660 has been used for testing the burning rates of furniture components and combinations of upholstery and coverings in small scale. The results have been used to predict burning rates of furniture in the full scale the furniture calorimeter as defined in NT Fire 032 [15.123].
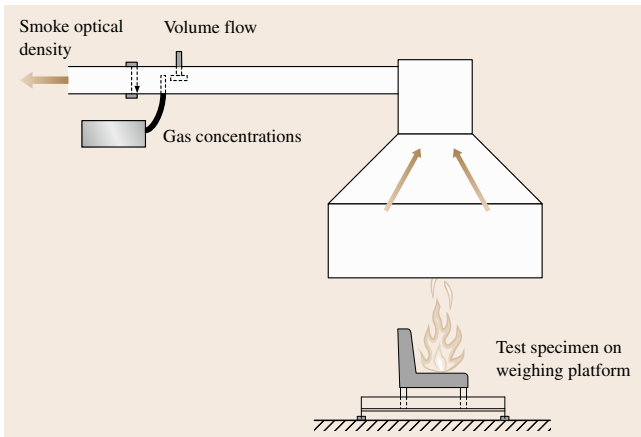
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