[VEHICLE ENGINEERING] [MEDICAL TECHNOLOGY] [PACKAGING] [ELECTRICAL&ELECTRONICS] [CONSTRUCTION] [CONSUMER GOODS] [LEISURE&SPORTS] [OPTIC]

Absorption of Water by Molded Plastics

Numerical Simulations Help to Describe and Understand Diffusion Processes

What does the simulation of a diffusion process have to do with the simulation of a temperature field? Simply put, they share the same differential equation. This property can be exploited in such a way that diffusion processes can be simulated with the aid of finite element programs. Such numerical simulation vividly reveals how such processes take place and how water absorption can influence the design of molded plastics.
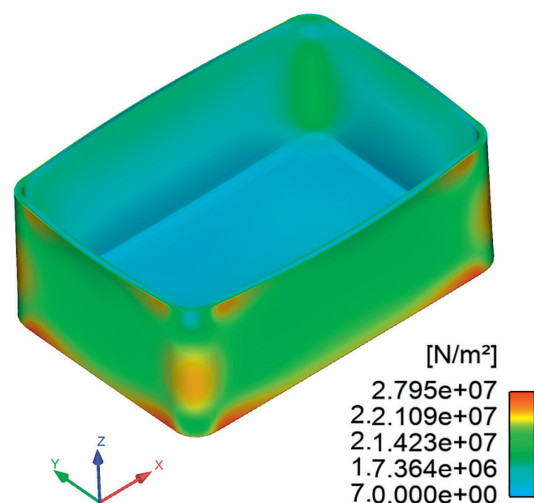
Test setup and simulation: How does a component behave after three years of water absorption? A simulation quickly provides information, e.g. about water saturation, deformation and (in the figure on the right) the von Mises equivalent stress Source: Merkle; graphic: © Hanser

A body will expand as a result of a rise in temperature. This is a well-known phenomenon. Far less well known is that a body will also expand (swell) upon absorbing a liquid, e.g. water, and will thus undergo a change in its mechanical properties.

This behavior is observed very readily in the polyamides class of polymers. Polyamide 6 and 66 absorb about 2.5 wt.% of water at room temperature and 50 % relative humidity; the water saturation point for these polyamides in water is about 8 wt.%. The material properties change markedly as a function of water absorption. The degree of water absorption is often termed the conditioned state.

Change in Mechanical Properties

Water absorption causes molded parts to swell, lowers their softening temperature (glass transition temperature), reduces their stiffness (modulus of elasticity) and decreases their strength. At the same time, their ductility and impact strength increase. Furthermore, diffusion processes can lead to internal constraints, e.g. as a result of concentration differences within the part. Since polyamides constitute the largest group of engineering plastics, examples of their use abound in, e.g. the automotive, construction industry (masonry ducting) [1], and electrical engineering industries.

Water absorption may be described as a diffusion process. Finite element programs capable of simulating deformations and stresses for any geometry and load conditions are a suitable means for calculating and measuring molded plastics. As many finite element programs do not model diffusion processes, recourse can be made to the heat transfer process (**see Box p. 44**) which is employed in classical temperature field calculation and can serve as an analogy. This approach makes it possible to describe the diffusion process with simple means and to factor it into the part design.

This paper explains this approach, from the obtaining of material valu- **»**

es to numerical simulation through to evaluation.

Standards and Guidelines

DIN EN ISO 62 [2] can be used for the experimental determination of the diffusion coefficient and the saturation value (degree of water absorption). The basic procedure is described below. It should be noted that there is a great deal of freedom with regard to the choice of specimen geometry. The coefficient of diffusion and the saturation value as properties of a material are largely independent of a specimen's geometry.

However, the change in absorption of water over time does depend on the specimen's geometry (**Fig. 1**). Therefore, whenever the water absorption as a function of time is specified in a material data sheet, the specimen geometry must also be specified – a rare occurrence in practice.

The determination of the diffusion coefficient according to DIN EN ISO 62
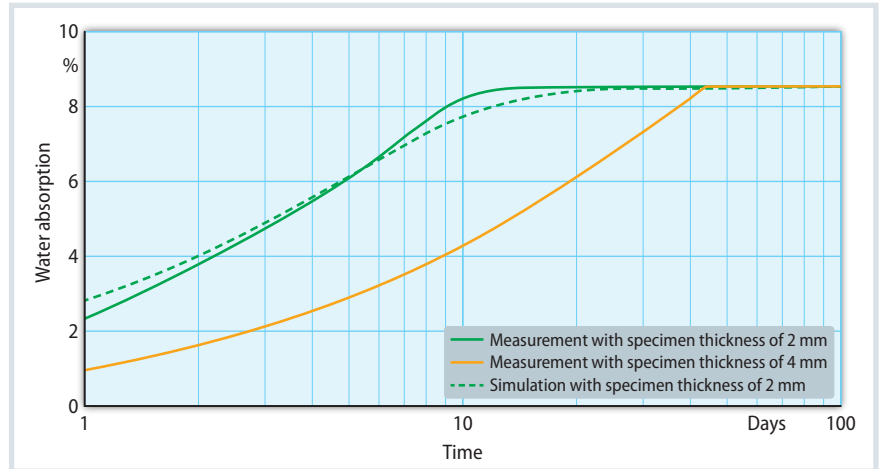

Fig. 1. Water absorption of polyamide 66 over time when aged in 40 °C warm water according to [3]: The change in water absorption over time varies with the thickness of the specimen, but the saturation value remains the same. A simulation conducted on a specimen thickness of 2 mm shows good agreement with the experimental curve Source: Merkle; graphic: © Hanser

requires at least two experimentally determined water-absorption values over time. Ideally, these are the degree of water absorption at 90 % and at 70 % of the saturation value.

Validation Illustrated with the Example of a Plate

A simple test specimen in the form of a plate (20 mm x 40 mm x 2 mm) made from unreinforced polyamide PA66 (conditioned state: dry) is immersed in water at a temperature of 40 °C and the change in water saturation over time is determined. The ideal experimental curve and also the expected result for PA66 are taken from [3]. In the first step, the diffusion coefficient is determined iteratively in accordance with Annex A.1 of DIN EN ISO 62 as being $1.02 \cdot 10^{-12}$ m^2/s. This compares with the diffusion coefficient stated in [3] of $0.9 \cdot 10^{-12}$ m^2/s. The experimental value is not exact, but is of the same order of magnitude and is sufficiently accurate. For a transient diffusion analysis, the density and the degree of water absorption at saturation are still required. The required material properties for a diffusion calculation are illustrated with an example in **Table 2**.

The definition of the underlying FE model provides for 40 hexahedral elements across the plate thickness in order that the spatial resolution across thickness and time is as exact as possible. In particular at the beginning of immersion, a large saturation gradient is established across the thickness of the plate, because the surfaces in contact with the water are the first to absorb the water, while the interior is still virtually dry. As saturation progresses, the gradient becomes smaller. At full saturation, all elements are saturated to the same degree.

Analogy between Diffusion and Heat Transfer

In principle, diffusion processes (mass transfer processes, too) and heat transfer processes are very similar. The corresponding differential equations are identical (**see Table 1**). The following material properties are needed for calculating a diffusion process:

- the matrix of diffusion coefficients D in $\frac{m^2}{s}$,
- the diffusion expansion coefficient β due to a mass absorption in $\frac{m^3}{kg}$ and
- the saturation value C_s in $\frac{kg}{m^3}$.

The essential result variables are

- the mass concentration C in $\frac{kg}{m^3}$ and
- the swelling behavior in the form of the elongation ε^d as a function of the mass concentration difference ΔC in $\frac{kg}{m^3}$.

By analogy, the following material properties are required for heat transfer calculations:

- the matrix of thermal conductivity coefficients λ in $\frac{W}{m\,K}$,
- the density ρ in $\frac{kg}{m^3}$ and
- the specific heat capacity c in $\frac{J}{kg\,K}$ and the thermal expansion coefficient a in $\frac{1}{K}$ arising from a temperature change ΔT in K.

In this case, the result variables are

- the temperature in T in K and
- the expansion ε arising from a temperature change ΔT in K.

	Diffusion	Heat Transfer
Steady state calculation	$J = -D\nabla C$	$q = -\lambda\nabla T$
Transient calculation	$\dfrac{\partial C}{\partial t} = D\nabla^2 C$	$\dfrac{\partial T}{\partial t} = -\dfrac{1}{\rho c}\lambda\nabla^2 T$
Expansion	$\varepsilon^d = \beta\Delta C$	$\varepsilon = a\Delta T$

Table 1.
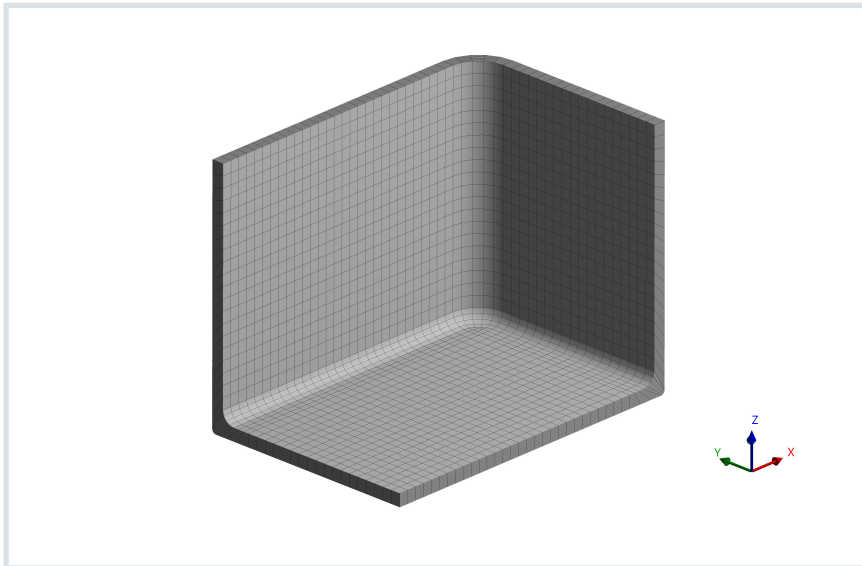Comparison of the equations for diffusion and heat transport

Source: Merkle

Fig. 2. FE model of the demonstrator: The meshing was carried out with ten hexahedral elements across the wall thickness. The more elements provided across the thickness, the better the transient diffusion process can be modeled. The simulations were carried out on a quarter model with symmetry boundary conditions © Merkle

For evaluation purposes, a mean degree of saturation is determined in the plate at each point in time. This allows the numerically determined results to be compared with the experimental results (**Fig. 1**) and provide very good agreement. This example of a validation is an impressive illustration of how a thermal FE analysis can be used to perform a diffusion simulation.

Demonstrator Part – An Open Housing

A molded part made of unreinforced PA66, measuring approximately 150 mm x 105 mm x 60 mm (open on one side) and having a wall thickness of 3 mm was subjected to numerical analysis. This housing (**Fig. 2**) is completely filled on the inside with water. The outside walls are in contact with a standard atmosphere (20 °C and 50 % relative humidity). No exchange with the environment occurs on the side in contact with the ground. A thermal FE analysis is conducted to study the behavior of the molded part as water diffuses into the polymer over time.

A concentration-dependent, multi-linear plastic law is used for the structural-mechanical calculation. This involves combining the true stress-strain curve with geometric non-linearity, i.e. taking large deformations into account. The structural boundary conditions are chosen such that additional constraints cannot arise. For simplicity, the influence of water absorption is the only load taken into account. In other words, the simulation neglects the dead weight of the structure and the hydrostatic pressure of the liquid.

The mechanical behavior of the material is defined as being a function of the degree of saturation. In this connection, stress-strain curves were determined by the Aalen University of Applied Sciences on polyamide 66 (PA66) tensile specimens at two different degrees of saturation (**Fig. 3**). The saturation values and the diffusion coefficient were determined at 20 °C.

In the FE model, ten hexahedral elements across the wall thickness were selected, a choice which proved to be sufficiently accurate in follow-up numerical analyses. The material is assumed to have been conditioned to saturation in a standard atmosphere and to have a water content of 2.7 wt. %.

Mathematically, water absorption reaches a steady equilibrium state after approx. three years, which corresponds to approx. 100 million seconds. **Figure 4** shows the water saturation, deformations and the resulting stresses over time. It can be seen that maximum deformation of about 7 mm is reached after about **»**

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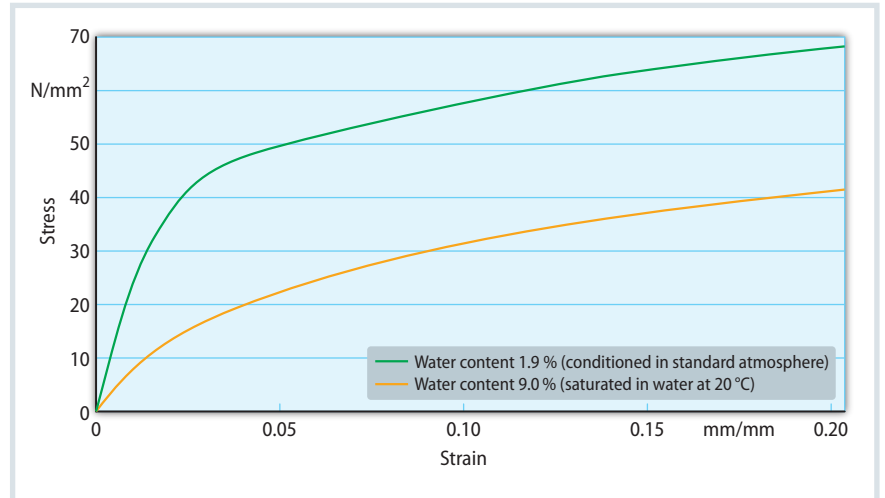## Service

References & Digital Version
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	Formula symbol	Unit	Value	Source
Density	ρ	$\dfrac{kg}{m^3}$	1130	[4]
Diffusion coefficient	D	$\dfrac{m^2}{s}$	$1.016421 \cdot 10^{-12}$	Determined from [3]
Water absorption at saturation	C_s'	%	8.53	[3]
Water absorption at saturation	C_s	$\dfrac{kg}{m^3}$	96.389	$= \rho C_s'$
Diffusion expansion coefficient	β'	-	0.2906	[5]
Diffusion expansion coefficient	β	$\dfrac{m^3}{kg}$	$2.57168 \cdot 10^{-4}$	$= \beta' \dfrac{C_s'}{C_s}$

Table 2. Material properties for PA66 immersed in water at 40 °C: these are required for a diffusion simulation Source: Merkle

116 days. This can be observed with the naked eye. In contrast, the maximum stresses only appear after three years. The stresses induced by swelling in the molded part reach a level that gives rise to plastic strain and thus permanent deformation. This effect should be considered when a molded part intended for use under comparable conditions is being designed.

Conclusion

This paper has demonstrated the possibilities afforded by numerically simulating diffusion processes in polymers. By analogy with heat transfer processes in thermal simulations, diffusion processes can be modeled in a wide range of finite element programs. It should be noted that the material properties must be available in a suitable form. DIN EN ISO 62 provides good reference values for the experimental determination.

With the aid of the demonstrator part of an open housing it was shown that swelling stresses may be caused by absorption of water – these should not be neglected and should be factored into the design of any plastic part. ∎

Fig. 4. Water saturation, deformation and stress over time (shown as a quarter model): Maximum deformation occurs after 116 days, while maximum stress in the steady state occurs only after 1157 days

Source: Merkle; graphic: © Hanser