

Elastomers in Drinking Water Contact – A Challenge

Author

Rainer Brandsch, Managing Director, SAFE+ Algorithmics GmbH · E-mail: rainer.brandsch@saferithm.com

Elastomers in contact with drinking water are subject to increasingly complex regulatory requirements. With the introduction of the KTW Evaluation Criteria (Umweltbundesamt, the German Federal Environment Agency) and the European Drinking Water Directive (European Commission), new challenges arise for manufacturers of elastomer components.

A particular challenge is posed by formulation-specific requirements. Where substances subject to a limit value (MTC_{tap} – maximum tolerable concentration at the tap) are employed in the manufacture of elastomer components, compliance of the product with these limit values must be demonstrated under conditions of use. Such evidence may be provided either by migration testing or by migration simulation (modelling).

This article sets out the potential of migration simulation in the context of the crosslinking reactions characteristic of elastomers, with due regard to the processing conditions applied.

Regulatory Framework

The legal requirements governing materials in contact with drinking water define, besides requirements on composition (formulation assessment, i.e. comparison against the positive list), requirements on the enhancement of microbial growth, requirements on water quality (odour, taste, turbidity, colouration), and formulation-specific requirements. For elastomers, the latter derive, among other things, directly from the crosslinking agent employed. Where peroxide crosslinking is used, both the peroxides themselves and their degradation products are listed with a limit value (MTC_{tap}). Where sulfur crosslinking is used, the accelerators and their degradation products are likewise listed with a limit value (MTC_{tap}).

Example of a permitted peroxide

(KTW-BWGL, Annex D.1.4.1.6 – Peroxides and coagents for peroxide crosslinking)

Peroxide: 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (CAS No. 78-63-7), $MTC_{\text{tap}} = 0.1 \mu\text{g/L}$

Degradation products:

tert-butanol, $MTC_{\text{tap}} = 500 \mu\text{g/L}$

tert-amyl alcohol, $MTC_{\text{tap}} = 0.1 \mu\text{g/L}$

2,5-dimethylhexane-2,5-diol, $MTC_{\text{tap}} = 0.1 \mu\text{g/L}$

2,2,5,5-tetramethyl..., $MTC_{\text{tap}} = 0.1 \mu\text{g/L}$

Above 0.4 % (m/m) in the formulation, additionally:

3,3,6,6-tetramethyl-1,2-dioxane, $MTC_{\text{tap}} = 0.1 \mu\text{g/L}$

di-tert-butyl peroxide, $MTC_{\text{tap}} = 0.1 \mu\text{g/L}$

Compliance with the limit values of the crosslinking agent as well as its associated degradation products and impurities must be demonstrated on the finished product under conditions of use. Migration testing, and equally migration modelling, of factory-made products is carried out in accordance with DIN EN 12873-

1:2014-09, whereby the appropriate migration cycles must be observed depending on whether the intended use is contact with cold, warm, or hot water. The migration results obtained must then be converted, via the application-specific conversion factor, into c^{tap} and compared against the MTC_{tap} .

Modelling versus Testing

Evidence that a product complies with a given limit value may be provided, on an equal footing, either by modelling (KTW-BWGL, Section 6.3.2) or by testing (KTW-BWGL, Section 6.3.1). Compared with testing, modelling requires additional information, namely (i) the material- or product-specific parameters needed for the model (either known or estimated), and (ii) the concentration of the substance in question within the product under assessment (c_0). The initial concentration (c_0) for the migration simulation can be determined in the material by extraction (the residual amount) or calculated from the amount originally added, provided the substance remains unchanged during manufacture and processing of the product.

The thermally induced decomposition of peroxides is, to a good approximation, a first-order reaction. For most peroxides, the kinetic parameters can be found in the respective technical data sheets.

Half-lives of 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane in chlorobenzene, e.g. from the technical data sheet of Trigonox 101:

0.1 hours at 156 °C (313 °F)

1.0 hour at 134 °C (273 °F)

10 hours at 115 °C (239 °F)

Half-lives determined in chlorobenzene or other media allow only an approximate estimate of the decomposition kinetics. Where the half-lives are instead determined by means of a Rubber Process Analyzer on materials taken from practice (cf. in this issue: Wrana, C., "From the KTW-BWGL to the DWD – Quo vadis"), the decomposition kinetics can be analysed under practice-relevant processing conditions and the kinetic parameters derived accordingly.

The result of simulating peroxide decomposition under processing conditions is, on the one hand, the residual amount of peroxide and, on the other, the amount of degradation products formed in the material. Combined with the polymer-specific constant for EPDM (determined within the framework of a project funded by figawa e.V.), the migration of the peroxide and its degradation products can be simulated in accordance with DIN EN 12873-1:2014-09.

Deduction of material diffusion properties (A_p' , τ)

***robust mean value and robust standard deviation
according to Algorithm A in ISO 13528:2015(E).***

✓ material specific constant at 23°C

$$A_p = 10,13 \ (\sigma = 0,89)$$

✓ material specific constant at 60°C

$$A_p = 9,19 \ (\sigma = 0,70)$$

$$A_p = A_p' - \tau/T \ [T \text{ in K}]$$

$$A_p' = 1.667$$

$$\tau = -2508$$

$$E_A = 66 \text{ kJ/mol}$$

$$D_p = D_0 \exp \left(A_p - 0.1351 \cdot M_r^{2/3} + 0.003 \cdot M_r - \frac{R \cdot 10454}{R \cdot T} \right)$$

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**=> modelling of barrier efficiency of elastomer layer (EPDM,
sulfur cross-linked) based on estimated diffusion coefficients**

Dr. Rainer Brandsch

saferithm

Fig. 1: Polymer-specific constant (A_p value) for EPDM from the figawa project, 2024

An experimental migration test in the laboratory would not be required. A particular feature of modelling is that it is, by design, conservative (overestimating), i.e. should the modeling indicate that a restriction is exceeded, the possibility of determining the migration experimentally still remains.

Simulation of Migration

Typical loadings of peroxide in the crosslinking of EPDM lie in the range of >1%. For the migration simulation, a loading of 1.5% is assumed. Typical processing conditions for peroxide-crosslinked EPDM compounds are, for example, 180 °C for a few minutes (e.g. 540 seconds) (cf. in this issue: Wrana, C., "From the KTW-BWGL to the DWD – Quo vadis"). Using these parameters together with the half-lives of the peroxide 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, a residual amount of 0.73 mg/kg is obtained for the peroxide in the EPDM compound. Where the material reaches a temperature of only 170 °C during the processing time, the residual amount of peroxide would instead be 275.94 mg/kg. Given that the migration of a substance from the elastomer is proportional to the residual amount, the lower processing temperature of 170 °C would accordingly result in a migration approximately 400 times higher.

For an elastomer component with a thickness of 2 mm, at the standardised surface-to-volume ratio of 5 dm⁻¹, a peroxide migration of $c_{\text{mod}} = 0.0015$ mg/L is obtained. For the migration simulation, the diffusion coefficient of the peroxide in EPDM, $D_p = 7.5 \times 10^{-10}$ cm²/s, was estimated by the Piringer method via the A_p value from the figawa project, the molecular weight of 290.44 g/mol, and a temperature of 23 °C. The partition coefficient between EPDM and water, $K_{p,w} = 225$, was estimated via the octanol/water partition coefficient of the peroxide ($\log P_{O/W} = 3.9$).

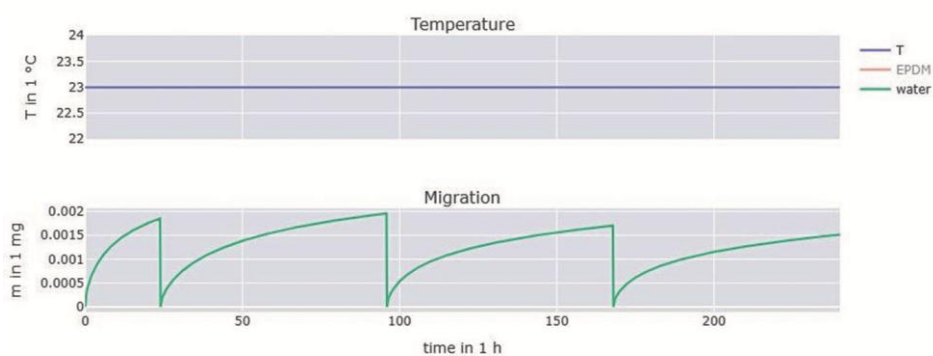


Fig. 2: Migration of peroxide (CAS No. 78-63-7) at 23 °C (cold water) according to DIN EN 12873-1

The migration result (c_{mod} from modelling, or c_{test} from testing) must be converted into a concentration at the tap, $c_{\text{tap}} = F_c \times c_{\text{mod}} / O/V / t$, under consideration of the conversion factor F_c appropriate to the application, by taking into account the surface-to-volume ratio O/V under consideration and the stagnation time t . In the present case, with a conversion factor $F_c = 1$ (fittings for pipes with $80 \text{ mm} \leq \text{ID} < 300 \text{ mm}$), a concentration at the tap of $c_{\text{tap}} = 0.1 \text{ } \mu\text{g/L}$ is obtained.

Peroxide-crosslinked elastomer components are usually post-cured (tempered) to remove volatile degradation products which, experience shows, tend to cause problems in the sensory testing of drinking water contact materials. As no robust data on the residual amounts of these degradation products were available at the time of writing, a migration assessment has been omitted at this point. In principle, the residual amount of the degradation products is accessible via the stoichiometry of peroxide decomposition; however, this leads to a strong overestimation of migration if the outgassing effected by post-curing is not taken into account.

Taking the entire manufacturing process of the elastomer component into account, it may be concluded that the MTC_{tap} limit value of the peroxide is met by the component in contact with cold water, provided manufacture proceeds in accordance with the assumptions made. Conversely, a limit value exceedance is to be expected in the case of incomplete crosslinking resulting from an insufficient processing temperature.

Conclusion and Outlook

From the temperature dependence of peroxide decomposition it can be deduced that the factor governing the migration potential is not the manufacturing process of the elastomer component as such, but rather the actual temperature/time profile applied during production of the product. In this respect, the thickness of the elastomer layer within the component may play a decisive role, since, with increasing thickness, a temperature profile develops within the component that, at a given processing temperature and with too short a processing time, can lead to incomplete crosslinking at the core of the elastomer layer. This, in turn, can result in elevated migration values, in particular an increasing trend in the measured values, such that the product would fail the migration test. Conversely, it follows that, in the manufacture of elastomer components, care must be taken to ensure that complete crosslinking is achieved through to the core of the elastomer layer under the processing conditions applied (temperature/time profile).

The reaction kinetics of sulfur-crosslinked EPDM compounds can likewise be determined by means of a Rubber Process Analyzer (cf. in this issue: Wrana, C., “From the KTW-BWGL to the DWD – Quo vadis”), rendering these, too, accessible to simulation of the reaction kinetics. Owing to the complexity of sulfur crosslinking, an autocatalytic model best describes the reaction kinetics. The numerical solution of the differential equation yields, as its result, the residual amount of the reactants – in particular the accelerators – and, on the other hand, the amount of degradation products formed within the material. With regard to the degradation products formed, it must be anticipated that a proportion of these become incorporated into the elastomer network. A systematic investigation of the concentration ratios within the

elastomer over the course of crosslinking is required in order to quantify the incorporated fraction of the degradation products.

CONTACT

R. Brandsch, SAFE+ Algorithmics GmbH, Göppingen, Germany

Email: rainer.brandsch@saferithm.com

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