From KTW-BWGL to DWD – Quo vadis

Well meant is not always well made

Claus Wrana, Compounds AG, Pfäffikon, Switzerland, e-mail: claus.wrana@compounds.ch

Abstract

Elastomer components in contact with drinking water are facing increasingly complex regulatory requirements. The introduction of the KTW-Bewertungsgrundlage (2025) and the European Drinking Water Directive (DWD, 2027) creates new challenges for manufacturers. This article examines the differences between the national and European positive lists, the impact on vulcanisation technology, and the economic consequences for production. It also presents technical details on crosslinking, the regulatory background, and possible solutions for the industry.

Regulatory framework

Requirements for materials in contact with drinking water have grown considerably more demanding in recent years. The KTW-Bewertungsgrundlage (KTW-BWGL) sets out clear requirements for the approval of elastomer components in Germany and becomes mandatory for all manufacturers from mid-2026. The European Drinking Water Directive (DWD) follows close behind, entering into force on 1 January 2027, with the aim of harmonising what has so far been a patchwork of national regulations and ensuring a uniform level of consumer protection across the EU.

A central element of both frameworks is the positive list: a register of which substances may be used in vulcanised rubber components, and the maximum concentrations at which these substances, and their reaction products, may be present in drinking water.

While the two lists share a broadly similar structure, the differences between the national requirements and the future European regulation are, in places, rather more significant than one might hope. Of particular concern is the introduction of an expiry date for listed substances: individual components are approved only until 2028 or 2031, after which reapproval must be sought, supported by comprehensive toxicological evidence.

This poses considerable challenges for the industry. Adding a new substance to the positive list is a slow and costly process, and one that holds little appeal for chemical manufacturers operating on a global scale. Unless the procedure changes, compliant compounds will become unavailable for the European market within the foreseeable future.

Vulcanisation as a key process

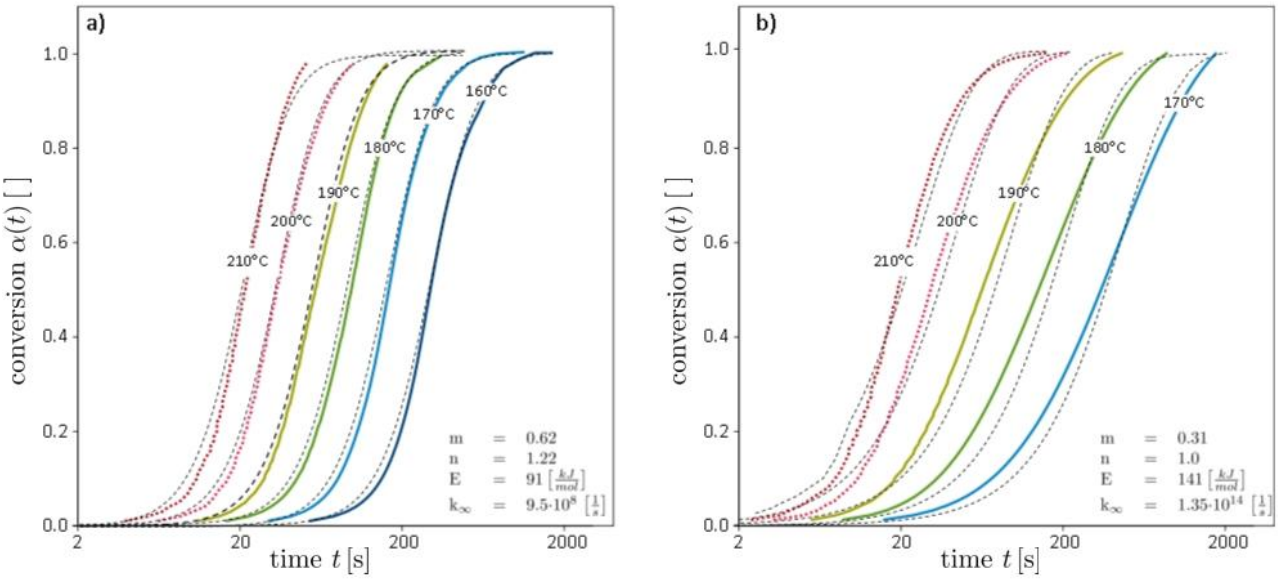
The production of rubber components requires vulcanisation, during which one or more chemical reactions take place. This gives rise to intermediate and end products that may migrate into drinking water and must therefore also be considered in the positive list. Only once vulcanisation is complete do the concentrations of these substances stabilise, allowing the migration test to be carried out reliably.

Vulcanisation is thus the decisive step for regulatory assessment, while at the same time influencing the mechanical properties and the economics of component manufacture. In practice, two crosslinking systems are used: peroxide-based and sulphur-based. The two differ in crosslinking kinetics and in the resulting material properties. The choice of system is generally governed by the manufacturing process and the intended application.

Large-volume components produced by injection moulding illustrate this well: economically viable production is only possible with sulphur-crosslinked compounds. The reason lies in the significantly shorter vulcanisation time compared with peroxide-based systems.

1. Comparison of peroxide- and sulphur-crosslinked compounds

Figure 1 shows the vulcanisation behaviour of two compounds at various temperatures. Compound T5821 is a carbon-black-filled, sulphur-crosslinked compound with a Shore hardness of 70 ShA; compound T9696 is its peroxide-based counterpart, likewise with a Shore hardness of 70 ShA. Measurements were carried out on a Bareiss RPA Ultra, following the procedure set out in ISO 6502.



F*ig. 1: Crosslinking curves of the sulphur-crosslinked compound T5821 (a) and the peroxide-crosslinked compound T9696 (b) at temperatures from 160°C to 210°C*

The figure plots the degree of crosslinking against time on a logarithmic scale, at various temperatures. The degree of crosslinking a is calculated from the measured torque using the formula

$$\alpha(t') = \frac{S(t') - S_{\mathrm{Min}}}{S_{\mathrm{Max}} - S_{\mathrm{Min}}} \qquad \text{Eq. 1}$$

where S(t') denotes the torque measured at time t – t_{Inc}, S_{Max} the maximum measured torque, and S_{Min} the minimum measured torque. The time t_{Inc} is regarded as the induction time; only once this temperature-dependent quantity has elapsed does the crosslinking process begin. Where reversion occurs – as is observed above all in sulphur-based systems at

temperatures above 190°C – this is not considered further here; a detailed treatment of the reversion effect is in preparation.

Because the specimens used in the Rubber Process Analyser measurements are thin (< 2 mm), the influence of thermal conductivity can be neglected and a constant specimen temperature assumed throughout the test piece. This does not hold for bulky components, where a temperature gradient can develop during vulcanisation, potentially leading to inhomogeneous crosslinking. The dashed lines in Fig. 1 represent calculated curves, obtained using an autocatalytic model.

$$\dot{\alpha}(t') = \frac{d\alpha(t')}{dt'} = K(T) \cdot \alpha(t')^m \cdot (1 - \alpha(t'))^n \text{ mit } K(T) = K_\infty \cdot e^{-\frac{E}{RT}} \qquad \text{Eq. 2}$$

Comparison of the measured curves with those calculated from the autocatalytic model in Fig. 1 shows that the model is well suited to the quantitative description of the crosslinking behaviour of both sulphur- and peroxide-crosslinked systems. The autocatalytic model can be applied in several ways. First, it allows the vulcanisation time in production to be optimised, by calculating the optimal – i.e. shortest – heating rate. This can be done either by estimating crosslinking on the basis of the temperature profile within the specimen during vulcanisation, or, more precisely though at greater effort, by simulating the crosslinking process using appropriate software based on the parameters of the autocatalytic model.

The crosslinking model can furthermore be combined with a simulation of migration behaviour. This would make it possible to express the concentration of decomposition products as a function of the degree of crosslinking, allowing the crosslinking conditions to be chosen so as to best satisfy the migration limits set out in the positive list.

In the manufacture of components with elastomeric parts, two quantities derived from the crosslinking curve are of central importance: the scorch time t_{10} and the cure time t_{90}. The scorch time t_{10} denotes the time at which 10% of full crosslinking is reached. In shaping processes, it is essential that the time required for shaping is significantly shorter than t_{10}; if this is not the case, the result is, at best, visible flow lines, and at worst incomplete mould filling and/or blistering in the component.

The cure time t_{90} denotes the time at which a degree of crosslinking of 90% is reached. Since elastomers have relatively poor thermal conductivity, demoulding is usually carried out at this point, with the component then continuing to fully cure as it cools. The cure time t_{90} is thus a measure of cycle time, and consequently a key quantity in the economic assessment of the crosslinking process: the shorter the cure time, the less energy is required, and the more parts can be produced per unit time. From the foregoing, it follows that, particularly in injection moulding, the highest possible scorch time t_{10} combined with the shortest possible cure time t_{90} is required.

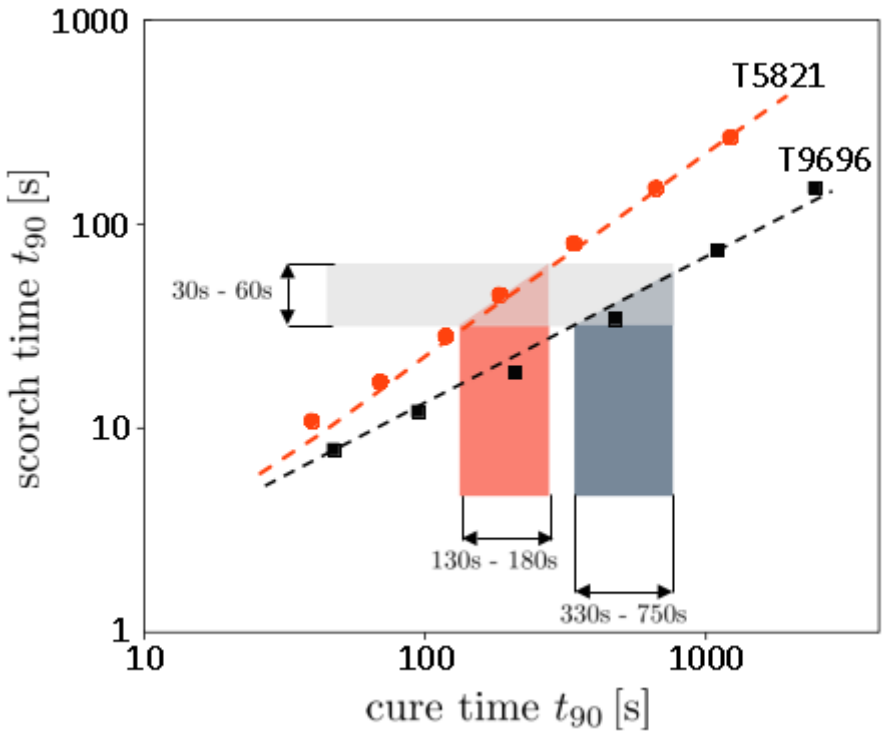


Fig. 2: Vulcanisation times t_{10} and t_{90} for sulphur- and peroxide-crosslinked systems

Fig. 2 shows the relationship between the scorch time t_{10} and the cure time t_{90} for the sulphur-crosslinked system T5821 and the peroxide-crosslinked system T9696. The symbols represent the measured data; the dashed lines were calculated using Eq. 2 and the parameters of both systems (see inset in Fig. 1).

When larger parts are produced by injection moulding, mould-filling times are typically between 20 s and 40 s. The scorch time should therefore be at least 30 s to 60 s. For scorch times in this range, the sulphur-crosslinked system shows t_{90} values between 130 s and 180 s, while the peroxide-crosslinked system shows t_{90} values between 330 s and 750 s. Peroxide-based compounds would therefore need to be cured for significantly longer in injection moulding – between 2.5 and 4 times as long as sulphur-crosslinked compounds.

Conclusion and outlook

Today, both sulphur- and peroxide-crosslinked compounds are used in the manufacture of elastomeric components in contact with drinking water.

The kinetics of peroxide crosslinking are governed by the decomposition of the peroxide, which can be influenced only to a limited extent. The curve shown in Fig. 2 therefore applies to all compounds crosslinked with this particular peroxide.

In sulphur-crosslinked systems, by contrast, the crosslinking kinetics can be significantly influenced through the choice of accelerator, allowing crosslinking to be tailored to the requirements of the specific process. Unfortunately, very few accelerators appear on the KTW-BWGL positive list, and only a small number are listed on the European list either. Their use is, moreover, so tightly restricted by very low migration limits that they cannot, in practice, be used at all.

The current situation with the German positive list is that it includes only two peroxides (one of which must be labelled as an SVHC) and a single effective accelerator for sulphur crosslinking. This accelerator is N-Cyclohexyl-2-benzothiazolsulfenamid (CBS), and only with it can a vulcanisation kinetics suited to injection moulding – and therefore economically viable production – be achieved. Were this accelerator no longer available, vulcanisation times would increase significantly as a result of less favourable crosslinking kinetics, making production by injection moulding too expensive. The consequence would be that these components are instead manufactured by manual compression moulding in countries with lower labour and energy costs.

The European list includes a somewhat larger number of accelerators, though all are subject to a time limit, generally set at 2031. Unless a reassessment is carried out by that date – itself an expensive, lengthy and far from straightforward toxicological evaluation – these accelerators may, from 2031 onwards, only be used in near-homeopathic quantities.

This stringent regulation is not a reflection of any demonstrated toxicity in the accelerators concerned, but rather of the fact that, for the largely globally operating manufacturers of most chemicals, the European market for drinking water applications is simply not large enough to justify the costly and demanding process required for inclusion on the positive list. Unless there is a substantial change to the approach for adding substances to the positive list – particularly with regard to the European list – we expect that, before too long, we will no longer be able to supply compliant compounds to the European market.

Certification under European law is considerably more complex than existing national regulations, and correspondingly more costly. The largest share of this cost falls on migration assessment, since the DWD requires that compliance with the positive list's limit values be demonstrated by measurement for every individual component. To simplify this process, we propose a methodologically reduced approach.

It is well established that migration values are influenced not by the manufacturing process itself, but by the course of crosslinking during production. It would therefore make sense to determine migration as a function of the degree of crosslinking or, ideally, to model it mathematically. To this end, we propose a joint project between industry and certification bodies, with the aim of deriving migration behaviour directly from the vulcanisation conditions. Should this approach succeed, there would no longer be any need to characterise the migration behaviour of every individual component; instead, it would be sufficient to demonstrate that crosslinking falls within a defined tolerance range.

This would not only allow for a considerably simplified and standardised assessment but would also significantly speed up production processes and substantially reduce costs.