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DEVELOPMENT WITHIN REACH

Polymer hardeners for epoxy resin systems enable development under REACH. By Wolf Meyer-Hevekerl, Dr Timo Rieckborn and Klaus Reinhold, Worlée-Chemie.

Polymer adduct hardeners make it possible, even under REACH, to develop individual solutions and thus respond flexibly to customer requirements. This article describes the statutory rules laid down by the European Chemicals Agency (ECHA), approaches to such solutions and the results achieved. Polymer adduct hardeners match the performance profile of conventionally produced adduct hardeners.

EU Regulation No. 1907/2006 on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) came into effect on 1 June 2007. While polymers are one type of substance that falls outside the scope of REACH, it must be remembered that the REACH definition of a polymer differs substantially from the scientific definition. Under REACH (Article 3 Paragraph 5) [1], a polymer is a substance which meets the following criteria:

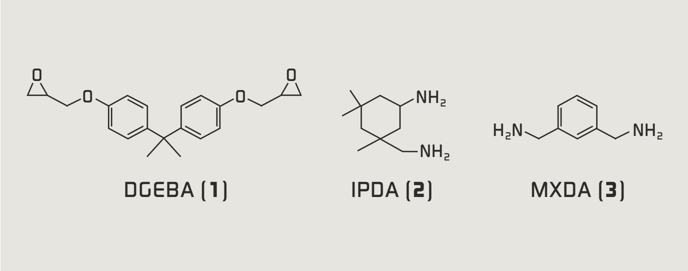
> Over 50 % of the weight of that substance consists of polymer molecules (see definition below), and
> The amount of polymer molecules presenting the same molecular weight must be less than 50wt% of the substance.
> A polymer is a sequence of at least three monomer units, which are covalently bound to at least one other monomer unit or other reactant. This is known as the (3M+1) rule.

If a substance is not a polymer and is subsequently introduced into a new process, it is deemed to be a monomer in that new process, even if it is composed of up to three monomer units. This is for example the case for standard bisphenol A epoxy resins that are based on bisphenol A diglycidyl ether (DGEBA (1) in *Figure 1*). The definition of what constitutes a 'monomer' is key to determining whether or not conventionally-produced adduct hardeners fall under the REACH definition of polymers.

CONVENTIONAL ADDUCT HARDENERS: STRUCTURE AND PRODUCTION

Conventional adduct hardeners, now often called "epoxy-resin-stabilised amines" or "epoxy-resin-adjusted amines," are generally produced in a process which begins with benzyl alcohol or extenders in a vessel. One or more amines are then added and homogenised. Finally, the epoxy resin components are incorporated to form the adduct. If more than one amine is used for adduct formation, several different adducts or mixed adducts are obtained. *Figure 2* illustrates this with the examples of adduct formation between bisphenol A diglycidyl ether (DGEBA (1)) with isophorone diamine (IPDA (2)) and with *m*-xylylene diamine (MXDA (3)). Such mixtures of different adducts cannot be registered under REACH. So, to ensure that REACH registration can take place, production processes have been switched to *in situ* adduct formation, as a result of which the amine hardeners no longer contain any mixed adducts. Once adduct formation is complete or the *in situ*

Figure 1: Monomers – as defined under REACH.



RESULTS AT A GLANCE

→ REACH will dramatically affect how development is managed in companies. A large number of adduct hardeners will disappear from the market.

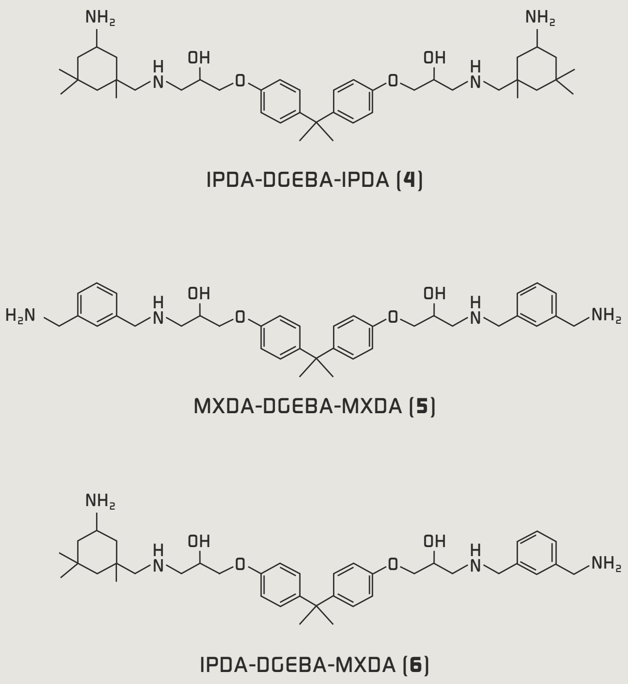
→ Companies will have to provide resources directed at replacing raw materials and consequently those resources will no longer be available for new developments and innovations.

→ Up to now, it was possible to deploy the entire range of amines in the development of epoxy resin hardeners to meet the requirements on mechanical properties, reactivity, viscosity and initial water and chemical resistance. That is no longer possible.

→ With polymer adducts, development possibilities in the field of adduct hardeners are largely retained. Their underlying technology makes it possible to still utilise all amines available for epoxy resin hardeners in the future and to formulate adducts with all bifunctional epoxy resin compounds.

adducts have been mixed together, amines, extenders and, in some cases, catalysts are added. The goal of adduct formation is a substantial reduction in the sensitivity of the amine hardeners to atmospheric humidity and carbon dioxide (carbamate formation). This secondary reaction leads to the formation of a white salt on the surface which is insoluble in water, impairs the appearance and causes possible adhesion problems between intermediate and subsequent layers.

Figure 2: Adducts formed by the chemical reaction of DGEBA with IPDA and MXDA.



IPDA-DGEBA-IPDA (4)

MXDA-DGEBA-MXDA (5)

IPDA-DGEBA-MXDA (6)

For the sake of completeness, in addition to conventional and polymer hardeners, blends (pure mixtures) and the theoretical possibility of an adduction with diglycidyl ethers (molecular weight > 700 g/mol) must be mentioned as well. Blends normally display low viscosity and have the significant disadvantage of a tendency towards carbamate formation during the curing process.

Adducts produced with diglycidyl ethers with a molecular weight >700 g/mol are either very highly viscous and therefore problematic in application or, in cases of appropriate dilution with amines, are likewise sensitive to carbamate formation *(Figure 3)*.

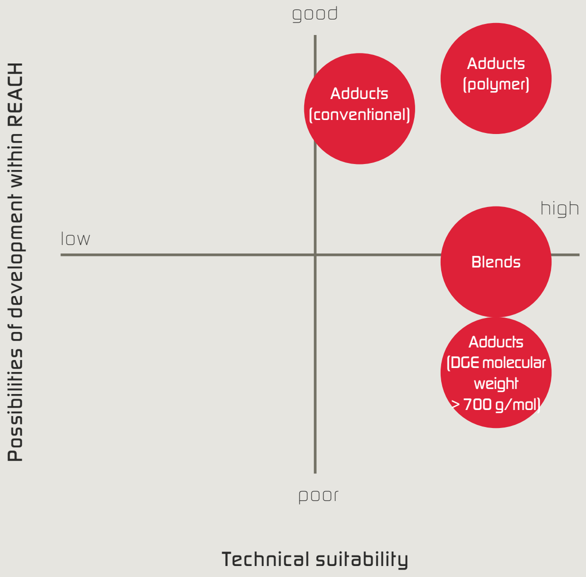
POLYMER HARDENERS: TYPICAL STRUCTURE

Polymer hardeners differ from conventional adduct hardeners mainly in that they are made not from mixed adducts, but rather from adducts which are composed of one or more polymers as specified in the ECHA's Guidance for Polymers and Monomers, dated April 2012. The dificulty here lies in converting these polymeric adducts, which can be very viscous, into functional epoxy resin hardeners.

In general, a polymer hardener has a structure consisting of four or five building blocks, with the polymer adduct forming the backbone. The desired performance profile is obtained by using amines, benzyl alcohol, extenders and accelerators. Additives may be incorporated to optimise particular properties in individual cases.

Important parameters other than viscosity are reactivity and surface properties. The key to developing suitable hardeners lies in striking a balance between the property profiles of the individual components. The polymeric nature of the adducts means that development of hardeners becomes much more challenging when it comes to reactivity and viscosity. The principles and experiences that proved so effective in traditional hardener development up to now no longer apply. In the case of VOC-free adducts, for example, it is much more difficult to substitute benzyl alcohol by extenders because it must be

Figure 3: Development possibilities within REACH vs. technical suitability.



assumed that the prerequisites concerning viscosity and reactivity have changed.

ANALYSIS TO VERIFY POLYMER STRUCTURE UNDER REACH

The determination as to whether or not an adduct constitutes a polymer substance under REACH can be illustrated by the chemical reaction of bisphenol A diglycidyl ether (DGEBA (1) in *Figure 1*) with *m*-xylylene diamine (MXDA (3) in *Figure 1*).

The possible compounds produced by the reaction of DGEBA with an excess of MXDA are listed in *Table 1*. Excess MXDA is a monomer and so does not satisfy the REACH (3M+1) rule. Nor is the rule satisfied by adduct MXDA-DGEBA-MXDA ((5) in *Figure 2*), which consists of 3 monomer units. The rule is only satisfied by the higher molecular adducts MXDA-(DGEBA-MXDA)$_2$, MXDA-(DGEBA-MXDA)$_3$ and MXDA-(DGEBA-MXDA)$_4$, which are made up of five, seven and nine monomers. For the reaction product to be a polymer substance within the meaning of REACH, the proportion of the three compounds MXDA-(DGEBA-MXDA)$_2$, MXDA-(DGEBA-MXDA)$_3$ and MXDA-(DGEBA-MXDA)$_4$ must exceed 50wt% in the product and none of the three adducts may constitute more than 50wt% of the product.

The analytical method selected for examining the reaction product was gel permeation chromatography (GPC). This method separates molecules by size as they migrate at different rates through a gel (screening effect) [2] [3] [4]. The stationary phase is a porous material, for which purpose modified polysaccharides, silica gels and polystyrene gels crosslinked with divinylbenzene are frequently used. A solution of the polymers is injected onto the separating column and the molecules diffuse into those gel pores which are large enough to accommodate them. This means that small molecules can enter all the pores of the stationary phase, where they are retained for long periods of time. Consequently, these molecules will be eluted last. Large molecules can only enter some of the pores, i.e. the larger ones, and so their retention time on the separating column is shorter. The various molecules therefore appear in the eluate in order of decreasing size. They are usually detected by measuring the refractive index of the eluate or the amount of UV/VIS light which it absorbs. Since GPC is not an absolute method, calibration with polymers of defined molecular weight distribution is necessary prior to the analysis.

For the reaction of DGEBA with MXDA, the samples to be separated by GPC were first acylated to prevent their having any undesirable affinity for the stationary phase. The acylation was performed in chloroform with an excess of acetic anhydride in the presence of pyridine. The

Figure 4: Development of Shore D hardness.

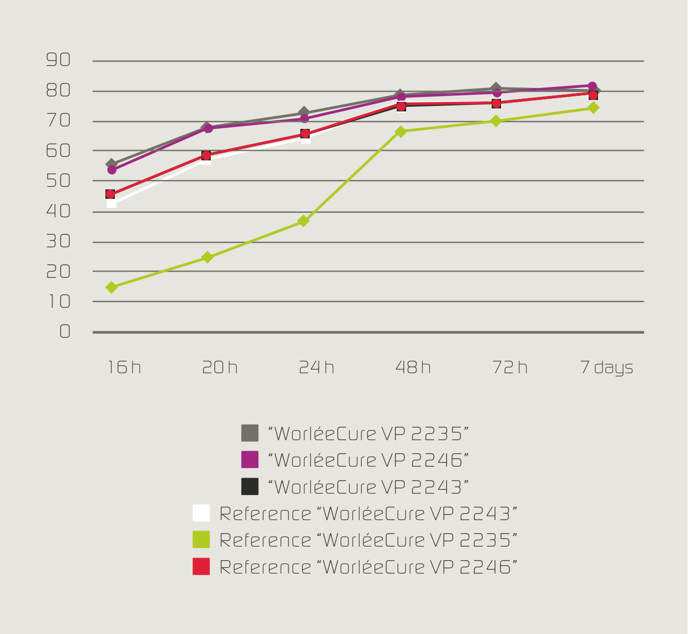


Figure 5: Development of pendulum damping hardness.

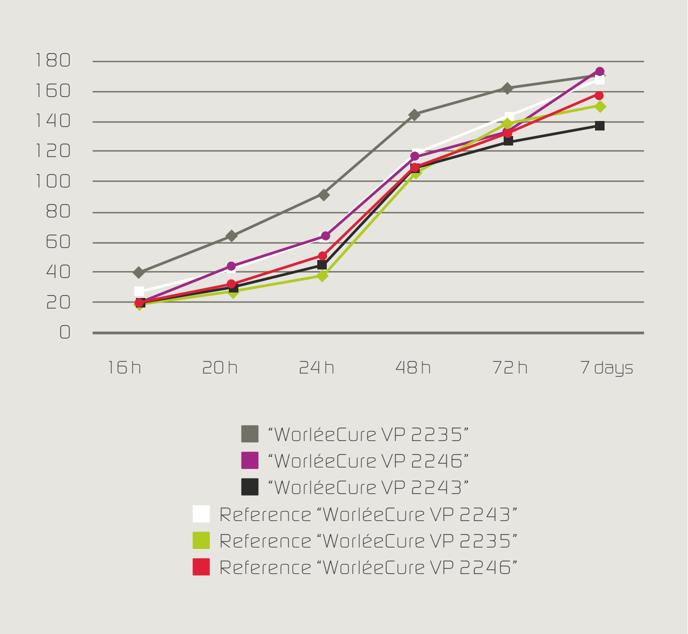
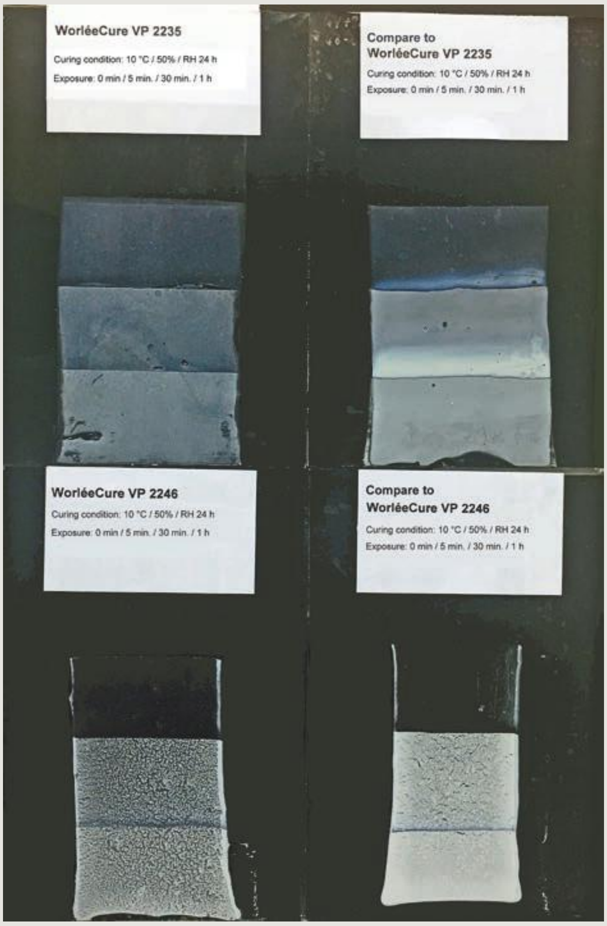


Figure 6: Initial water resistance.



samples were dried under vacuum to remove all volatile components. They were then prepared in tetrahydrofuran. Polystyrene crosslinked with divinylbenzene (PS-DVB) served as the stationary phase and a polystyrene standard was used for calibration. Tetrahydrofuran acted as the mobile phase. The GPC was conducted at 40 °C and detection consisted in measuring the refractive index of the eluate and determining the level of UV/VIS absorption with a UV/VIS photodiode array.

Figure 7: Chemical resistance based on weight increase.

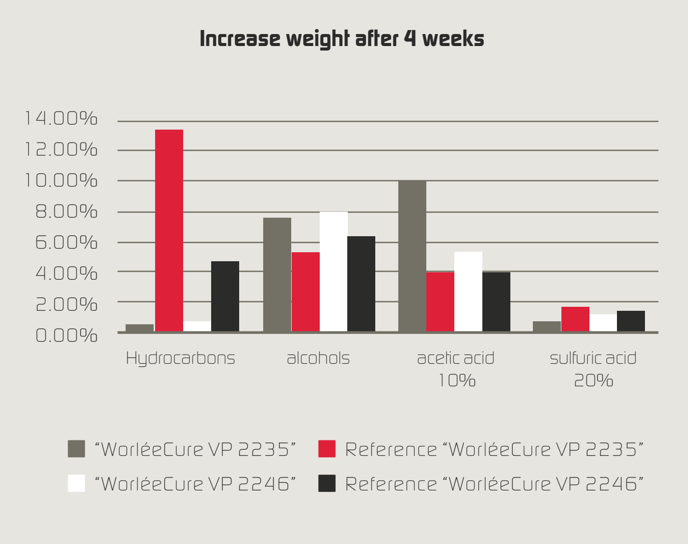


Table 1: Products of the reaction of DGEBA with MXDA.

Compound	Number of monomer units (M)	(3M+1) rule
MXDA	1	not satisfied
MXDA-DGEBA-MXDA	3	not satisfied
MXDA-(DGEBA-MXDA)$_2$	5	satisfied
MXDA-(DGEBA-MXDA)$_3$	7	satisfied
MXDA-(DGEBA-MXDA)$_4$	9	satisfied

Table 2: Viscosities of epoxy resin hardeners.

Epoxy resin hardener	Viscosity in mPa s
"WorléeCure VP 2235 "	460 – 660
"WorléeCure VP 2235" reference	200 – 400
"WorléeCure VP 2246 "	120 – 220
"WorléeCure VP 2246" reference	130 – 230
"WorléeCure VP 2243"	800 – 900
"WorléeCure VP 2243" reference	250 – 450

The GPC analysis showed that the three adducts MXDA-(DGEBA-MXDA)$_2$, MXDA-(DGEBA-MXDA)$_3$ and MXDA-(DGEBA-MXDA)$_4$ were present in a proportion greater than 50wt% of the reaction mixture. None of the three adducts exceeded 50wt% in the product. The reaction product thus met the definition of a polymer substance under REACH.

POLYMER HARDENERS VERSUS CONVENTIONAL EPOXY RESIN HARDENERS

Viscosity

The newly developed products can give rise to an increase in viscosity, but other properties remain the same. This marks a substantial change relative to conventional epoxy resin hardeners, as shown in *Table 2*.

Hardness development

The development of hardness was assessed by measuring the Shore D hardness and the pendulum hardness in a standard climate. The A component was an unfilled A/F epoxy resin with C12-C14 alkyl glycidyl ether. The Shore D hardness was measured on test specimens which were at least 3 mm thick and were hardened at 20 °C and 50 % relative humidity. As *Figure 4* shows, in thick layers, the new products harden at a rate comparable to that of commercial hardeners. One exception is “WorléeCure VP 2235”, which already has a much higher Shore D hardness after just 16 hours. Pendulum damping was measured on 200 µm thick films on glass which were hardened at 20 °C and 50 % relative humidity. As shown in *Figure 5*, the new products and the conventional hardeners exhibit comparable hardening behaviour.

Initial water resistance

Differences in initial water resistance were detected by first hardening 200 µm thick layers on glass for 24 hours at 10 °C and 50 % relative humidity and then immersing individual areas in water for 5 min, 30 min, and 1 hour. Various levels of carbamate formation were identified afterwards. As *Figure 6* shows, the results for the polymer hardener on the left and the conventional hardener on the right are comparable. Closer examination reveals that the polymer hardeners seem to have a somewhat lower tendency to form carbamates in this test.

Chemical resistance

Chemical resistance was determined by conditioning specimens in suitable test liquids (media groups No. 4, 5, 9 and 10 as per Deutsches Institut für Bautechnik, DIBt, the technical authority for the German construction industry) for up to four weeks. Weight increase then served as the criterion for chemical resistance. Differences in the chemical resistance of the samples can be seen in *Figure 7*. The polymer hardeners exhibit less weight increase than the conventional hardeners as regards resistance to sulfuric acid and especially hydrocarbons. The opposite is true for alcohols and acetic acid.

UV stability

The UV stability of individual epoxy hardeners was tested by irradiating the samples for 100 hours (340 nm and 182.9 kJ/m^2) in a xenon test chamber. The samples comprised 200 µm thick layers on glass. A standard bisphenol A resin (epoxy equivalent weight: 187) acted as the crosslinking resin. As shown in *Figure 8*, the polymer hardeners exhibit greater light stability than the conventional hardeners when tested against the yellowness index.

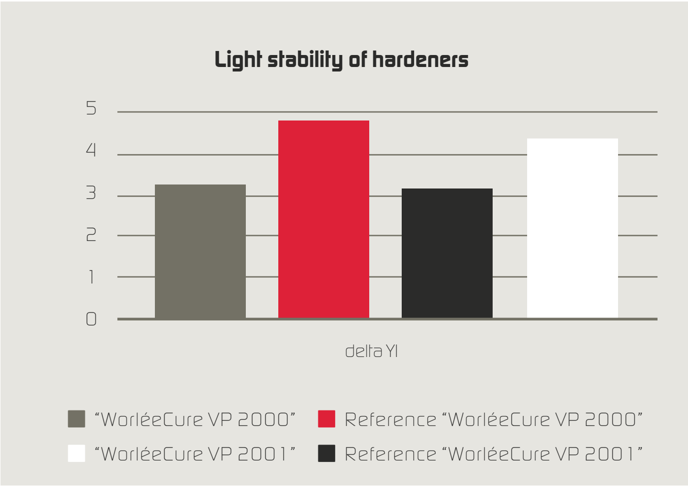
Behaviour towards additives

As regards improving the properties in a solvent-free system, a combination of defoamer “WorléeAdd 6235” and a surface additive proved to be particularly suitable. In comparative tests, this additive delivered the best performance with the new polymer hardeners.

SUMMARY OF THE IMPACT ON PRODUCT DEVELOPMENT

REACH will dramatically affect how development is managed in companies. A large number of adduct hardeners will disappear from the market. Research and development departments will have to develop suitable alternatives if existing product ranges are to remain available for a wide array of applications in the future. Niche products will be affected most of all, i.e. those hardeners which offer solutions to highly specific problems. The full extent of the challenge facing development departments will only emerge over the next few months. But even now there can be no doubt that the number of development projects and the amount of development work will rise significantly. Companies will have to provide resources directed at replacing raw materials and consequently those resources will no longer be available for new developments and innovations. For example, many adduct hardeners contain adducts which are not based on isophorone diamine (IPDA) and bisphenol A diglycidyl ether (DGEBA), but rather contain bisphenol F diglycidyl ether (DGEBF) or *o*-cresyl glycidyl ether as an adduct-formation partner (instead of DGEBA). These adducts are not REACH-registered and must therefore be replaced by registered substances. The only adducts currently available for this purpose are the aforementioned adduct formed by isophorone diamine and DGEBA and that formed

Figure 8: Comparative changes in yellowness index.



> “The challenge lies in achieving a balanced adducthardener formulation.“

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3 questions to Timo Rieckborn

Do you believe that completely new REACH-compliant adducts can be developed in the near future? *In contrast to the case for conventional adduct hardeners, we believe that it is this very point which offers great potential for polymeric adduct hardeners, as there is no REACH registration process required. The expected costs of registering under REACH and the time involved can have the effect of pre-empting development work on new adducts.*

How can R&D continue despite registration costs? *Development work will be dictated to a massive extent by the cost-benefit ratio. In the case of polymeric adduct hardeners, there are no registration costs to be borne and thus solutions tailored to customer requirements can continue to be developed.*

Comparing polymer to conventional adducts, where are the most significant deficits? *Polymeric adduct hardeners have higher viscosities and altered reactivities, and so the challenge lies in achieving a balanced adduct-hardener formulation. One such example is the development of VOC-free adduct hardeners.*

by *m*-xylylene diamine (MXDA) and DGEBA. This example clearly illustrates how great the challenge is. At the same time, the restriction to just three adducts greatly hampers the development of new solutions to this problem. Up to now, it was possible to deploy the entire range of amines in the development of epoxy resin hardeners as a way of meeting the requirements imposed on mechanical properties, reactivity, viscosity and initial water and chemical resistance. That is no longer possible. Now, any as yet unregistered substances first have to be registered. This raises the question as to who will bear the costs of registration. This issue will cause many projects to fail from the outset.

Development processes which previously concentrated on technical feasibility and were able to draw on a broad base of raw materials will now be severely constrained in their attempts to achieve results. This will make development work much more difficult and in many cases will have adverse effects not only on the performance delivered by the solutions, but on development times as well.

With polymer adducts, the development possibilities in the field of adduct hardeners are largely retained. The technology makes it possible to still utilise all amines available for epoxy resin hardeners in the future and to formulate adducts with all bifunctional epoxy resin compounds. Laboratory resources can thus continue to be deployed effectively on the development of technical solutions. Hardeners which contain unregistered adducts can be replaced by polymer adduct hardeners. In this way, the properties can largely be retained in most cases, and companies' development departments can use their time more profitably. Polymer adduct hardeners are an efficient way to develop innovative, tailor-made solutions and to market them successfully in the future.

LITERATURE

[1] ECHA Guidance for monomers and polymers, Version 2.0, ECHA, April 2012.
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[3] Bernd Tieke, Makromolekulare Chemie, 3rd Ed., WILEY-VCH, Weinheim, 2014.
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