ANCAMIDE® 2842 & 2861
EVONIK'S FLEXIBLE EPOXY HARDENERS

Figure 1: Application example of flexible epoxy metal coatings

MARKET NEED FOR FLEXIBLE EPOXY SYSTEMS

Epoxy resins cured by amine hardeners are often first choice in coating and adhesive applications, especially when excellent durability is required. The curing reaction forms a dense epoxy-amine network which leads to exceptional mechanical and chemical stability and allows for an extended service life. This contributes to reduced maintenance work and lower downtime costs, thus also fostering sustainability.

Although the high cross-linking density allows for high mechanical strength and chemical resistance, it also bears the drawback of brittleness, when it comes to mechanical impact and stress. For various end applications there is a clear market need for higher flexibility and elongation:

In some concrete protection and flooring applications coatings are exposed to moderate or heavy duty service and frequent movement and stress; especially in crack bridging, bridge deck overlays or joint sealings. Tensile elongations up to 100 % are needed for these systems, including high fatigue resistance. In metal coatings the requirements are less demanding for tank linings or flexible industrial coatings (see example in **Figure 1**), but still in a range of up to 50 % elongation while maintaining overall good anti-corrosive and chemical resistance properties. The highest flexibilities are required for adhesive, potting and encapsulation applications to ensure mechanical and thermal shock resistance as well as crack bridging when bonding various substrates. A high bending strain and elongation of up to 100 % are mandatory for these applications.

The flexibility can be adjusted by the binder system which determines the main coating or adhesive properties. One approach towards flexibilization is the addition of flexibilizing agents such as non-reactive plasticizers, high molecular weight polymers with flexible chains or CTBN (carboxy-terminated nitrile butadiene) rubbers. However, this is often achieved at the expense of other formulation properties such as adhesion or chemical resistance.

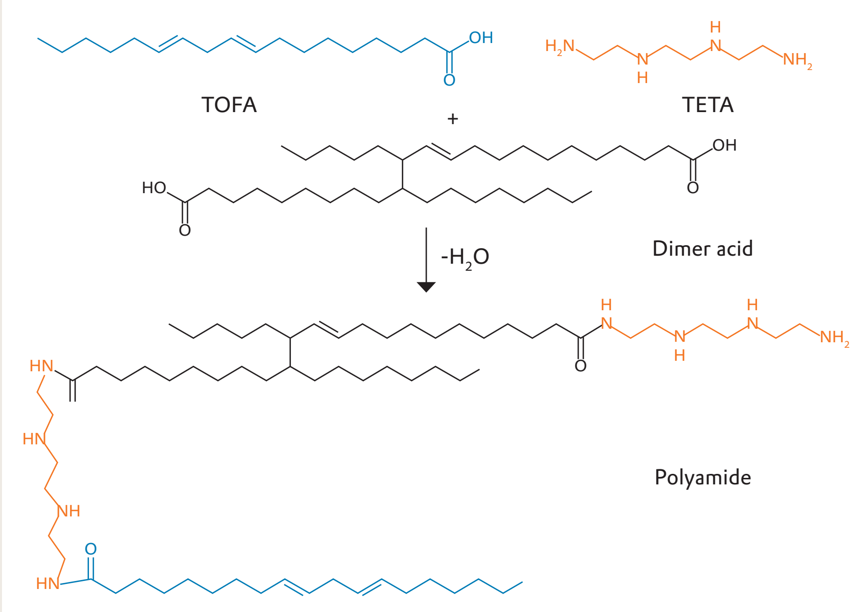
This can be overcome by including flexible moieties directly into the backbone of the epoxy hardener. Evonik offers several amine curing agents, including two new developments, which provide excellent flexibility while maintaining beneficial properties of typical epoxy systems.

FLEXIBLE HARDENERS BASED ON POLYAMIDE TECHNOLOGY

Evonik's new flexible hardeners are based on polyamide chemistry which is an established technology in the market.

Polycondensation of higher functional amines such as triethylenetetramine (TETA) with dimer fatty acids leads to polyamides. Addition of tail oil fatty acid (TOFA) as a chain stopper helps to control the molecular weight of the product (**Scheme 1**).

Scheme 1: Polycondensation of TETA with Dimer fatty acid using TOFA as chain stopper.



The long alkyl chains from the fatty acids in the polyamide backbone already provide some flexible character. Polymer properties such as viscosity and functionality can be controlled and further finetuned by changing the monomer ratios. In addition, the hydrophobic fatty acids help to achieve good corrosion resistance. Amide and unreacted amino groups lead to good adhesion to metal panels and other substrates.

The basic characteristics of polyamides are excellent corrosion and good weathering resistance while having a long pot life and high viscosity. They are usually diluted with solvents for having more freedom of formulation.

Additional flexibility can be introduced by using other building blocks such as proprietary flexible amine monomers which belong to Evonik's broad portfolio of specialty amines. By replacing highly functional low molecular weight monomers such as TETA by flexible amines the flexibility of the resulting epoxy formulation can be significantly increased. Both new polyamide developments provide another benefit: They can be formulated with standard liquid epoxy resins instead of more complex solid epoxy resins dissolved in solvents. The flexible hardeners cured with Bisphenol A epoxy resin provide good surface properties without adding additional volatile solvents or plasticizers to the formulation. The final properties of the binder system can easily be further adjusted by variation of the resin part, e.g. by using Bisphenol F liquid epoxy resins or additional reactive diluents.

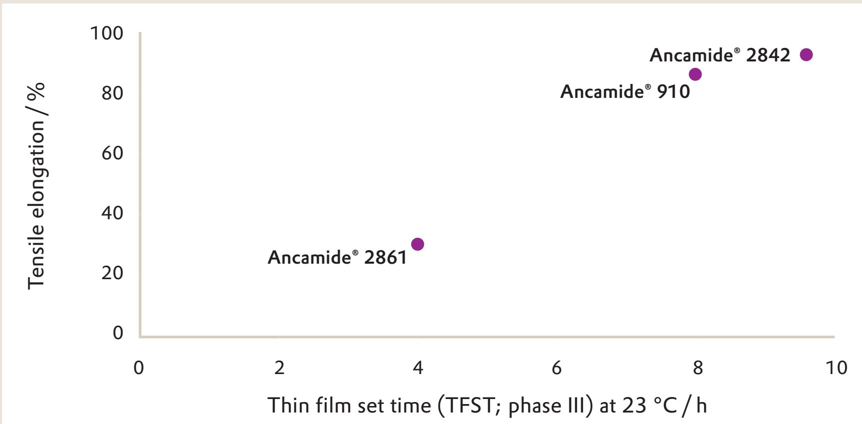
POSITIONING OF THE NEW GRADES IN THE FLEXIBLE HARDENER PORTFOLIO

Ancamide® 910 is an established epoxy hardener recommended for flexible applications. With the recent new developments the portfolio has been further extended. **Figure 2** shows that reactivity (related to thin film set time) and flexibility (related to tensile elongation) vary over a broad range which helps the customer to pick a tailor-made grade for the specific end application.

Ancamide® 2842 has been developed for use either as a sole curing agent or as a modifier for applications that require exceptionally high elongations. It is an ideal choice for electronic potting, encapsulation compounds and two-component adhesive formulations.

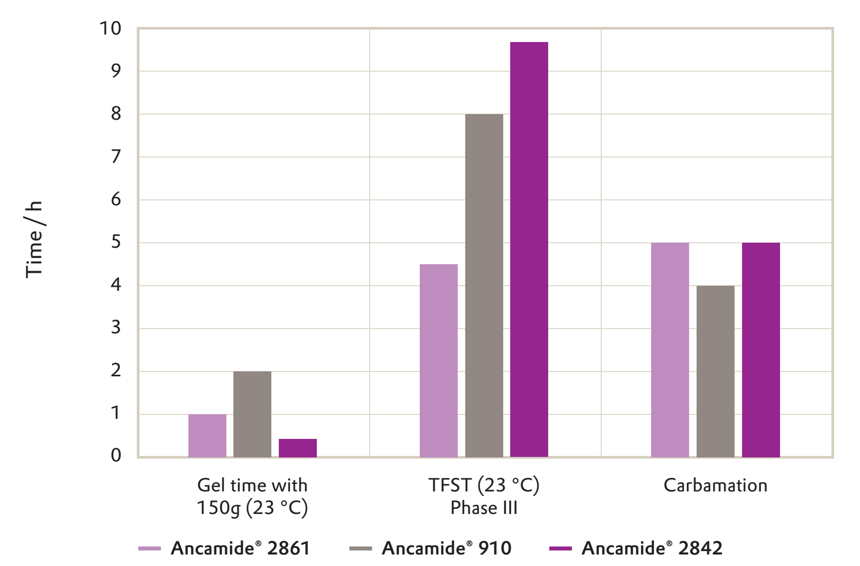
On the other hand, Ancamide ® 2861 has been designed for use in flexible metal primers and floorings, especially at low temperatures. Compared to both Ancamide®

Figure 2: Broad variation of flexibility and reactivity within the flexible hardener portfolio.



910 and Ancamide® 2842, this grade offers considerably higher reactivities even at lower temperatures. As measured by thin film set time (150 µm wet film thickness (WFT)), cure speed is more than doubled. Although this can be only achieved at the expense of flexibility, tensile elongation is still at a high level of 30 %. Additional features of Ancamide® 2861 include good balance of reactivity and pot life and excellent water-spot resistance. This is achieved by using Evonik's new multifunctional polycyclic Mannich base which is free of phenols, formaldehyde, and any other harmful raw materials. This ensures not only good acceleration of the epoxy-amine reaction but also a beneficial classification and labeling of the product.

Figure 3: Gel time, thin film set time and carbamation resistance of the hardeners cured with liquid Bisphenol A epoxy resin.



BASIC HARDENER PROPERTIES

Table 1 lists some basic properties of the three flexible polyamide hardeners.

Ancamide® 2842 has to be used at the same loading level as the established Ancamide® 910. In contrast, Ancamide® 2861 exhibits a higher amine functionality and can therefore be used at lower levels which helps to lower its cost-in-use.

The lower hardener viscosities of Ancamide® 2842, and especially Ancamide® 2861, allow for more freedom to formulate the final coating or adhesive when adding e.g. fillers and formulation agents.

All three grades show a yellow to amber color tone which is typical for polyamides. Ancamide® 2861 has a typical color of Gardner 6 which is significantly brighter than Ancamide® 910.

FORMULATION PROPERTIES

For the following reactivity test the epoxy curing agents are converted stoichiometrically 1:1 with standard bisphenol A liquid epoxy resin, having an average epoxy equivalent of EEW = 190.

The reactivities of the three flexible hardeners vary over a broad range which also influences their pot life. Pot life has been determined by gel time measurements of 150 g mixture using a gelation timer (ISO 9514): As shown in **Figure 3**, Ancamide® 2842 exhibits a limited gel time of 25 minutes at 23 °C whereas Ancamide® 2861 and Ancamide® 910 provide long gelation times and thus broad application windows of one and even two hours, respectively.

The cure speed was assessed by the thin film set time (TFST) measured by the Beck and Koller method (ASTM 5895-20 and DIN ISO 9117-4). Phase 3 is reached where the stylus has risen out of the film and rides on the surface, leaving only a mark without disrupting the body of the film, which can be correlated to touch-to-dry (ASTM D1640). Whereas Ancamide® 910 and Ancamide® 2842 exhibit comparably long dry times, the reactivity of Ancamide® 2861 is more than doubled. This allows not only for faster return to service but also for a reduction of curing temperature.

The carbamation resistance test was conducted on black Leneta charts according to ISO 2812-3 method. The coating was applied at 150 µm thickness. Either a water saturated cotton patch was placed on the cured coating or water dropped on the film then covered with a watch glass to prevent evaporation. The appearance of the coating was judged after given testing time in a scale of 1 to 5, with 5 being the best showing no effect, and 1 being the worst with a white surface. Carbamation resistance benefits from higher cure speed but also from the hydrophobicity and specific chemical structure of the polyamides. All three hardeners show good carbamation resistance at ambient temperatures with values of 4, respectively 5.

The fast cure speed of Ancamide® 2861 also leads to a fast development of shore D

Table 1: Basic properties of flexible hardeners

	Unit	Ancamide® 2842	Ancamide® 910	Ancamide® 2861
Amine equivalent (AHEW)	–	230	230	170
Parts per hundred (phr) with standard liquid Bisphenol A resin	–	123	123	90
Typical Color	Gardner	10	8	6
Appearance	–	amber	amber	clear
Viscosity (25 °C)	mPa*s	3200	6000	900

hardness measured according to ASTM D2240. After 24 hours at room temperature respective formulations are tested to determine the indentation hardness by means of durometer. The approximately 18.5 g pucks with 5 cm diameter and 1 cm thickness reached a shore D hardness of 69 which is considered as a good value for floor coating applications. In contrast, formulations based on Ancamide® 910 only reached a shore D hardness of 57 after 7 days at room temperature. This means that curing does not only take much longer but also the fully cured system exhibits less hardness. Formulations based on Ancamide® 2842 even needed post-cure at 80 °C for two hours to reach the minimum level to be walkable, corresponding to shore D 60.

Therefore, Ancamide® 2861 is the ideal choice for flexible floor coatings that benefit from an early shore hardness development, with no need for an extra step of post cure to reach a good level of shore hardness 69D after one day at room temperature.

ANCAMIDE® 2842 FOR ADHESIVE APPLICATIONS OF TEMPERATURE-SENSITIVE MATERIALS

Among the three flexible hardeners, Ancamide® 2842 exhibits the highest elongation which makes it a promising candidate for 2K adhesive applications. For further investigation of the cure profile, dynamic scanning calorimetry (DSC according to DIN EN ISO 11357) tests at a heating rate of 10 K/min were performed on formulations based on Ancamide® 2842 in comparison to Ancamide® 910.

At full through cure (second heating cycle), a glass transition temperature (Tg) of 28 °C is achieved which is on a comparable level to formulations based on Ancamide® 910 (25 °C). Due to its slower reaction kinetics, Ancamide® 2842 offers the benefit of lower exothermic heat flow which is decreased from 260 J/g to only 180 J/g. This further broadens the application area for this hardener. Releasing of heat upon curing avoids deformation or damage of the materials that are bonded. This applies for temperature-sensitive materials with low glass transition temperatures such thermoplastics or some composite materials.

To test the adhesion and bonding strength, lap shear strength of formulations with Bisphenol A resin were tested in the absence of any further additives on various substrates (**Figure 5**). All substrates were sanded prior to bonding; sample preparation and measurement were performed according to ASTM D1002. Similar or slightly higher lap shear strengths at high levels were observed on aluminum (Al), cold rolled steel (CRS), as well as polycarbonate (PC) and acrylonitrile-butadiene-styrene (ABS). All panels showed an adhesive failure, except for ABS which exhibited a substrate failure.

COMPARISON OF MECHANICAL PROPERTIES

The mechanical properties of the flexible hardeners were compared by tensile, flexural and compressive tests as well as Charpy impact strength tests (**Table 2**). None of the fully cured test specimens showed any failure in the tensile, flexural or compressive test. When applying yield strengths beyond the elasticity modulus, the test specimens are plastically deformed. This means that test specimens remain permanently elongated and do not return to the initial length, even if the force is completely relieved.

Due to its higher cross-linking density, the formulation based on Ancamide® 2861 provides more strength. This comes at the expense of reduced flexibility compared to the other two products, while still being extraordinary flexible for an epoxy system. This is also reflected in the Charpy test which resulted in destruction of the test specimen based on the more brittle Ancamide® 2861 whereas no break was observed for the other two hardeners. The broad variation demonstrates that, depending on the requirements of the final application, a suitable flexible hardener can be chosen from the three grades.

For metal coating applications (**Table 3**), the flexibility of thin films (dry film thickness 110 – 130 µm) on steel panels was assessed by impact resistance tests, mandrel

Figure 4: DSC Measurement

Curing reaction measured by DSC	Unit	Ancamide® 2842	Ancamide® 910
Onset temperature	°C	50.2	70.7
Exothermic peak	°C	98.1	118.9
Exothermic heat flow	J/g	179.7	261.2
Tg second scan	°C	28.3	25

Figure 5: Lap shear strength of Ancamide® 2842 and Ancamide® 910 on various substrates.
* Indicates curing at 40 °C for 24h followed 2 h at 80 °C.

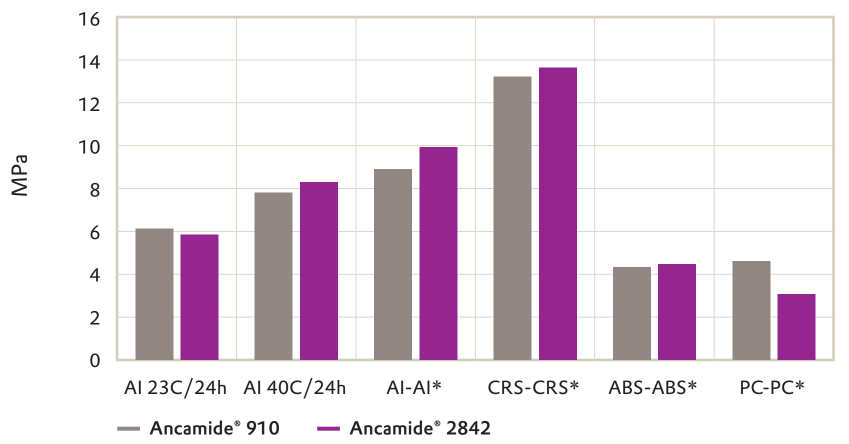


Table 2: Mechanical properties

	Method	Unit	Ancamide® 2842	Ancamide® 910	Ancamide® 2861
Tensile Strength	DIN EN ISO 527	MPa	11,6	9,5	26,5
Tensile Modulus		MPa	24,1	25,6	1680
Tensile Elongation		%	93,4	87,1	31,1
Flexural Strength	DIN EN ISO 178	MPa	1,05 (max)	1,15 (max)	51,6
Flexural Modulus		MPa	26,7	27,6	1620
Compressive Strength	DIN EN ISO 604	MPa	410	416	351
Compressive Modulus		MPa	33	48	1667
Charpy test 1eU	DIN EN ISO 179	kJ/m²	151	129	79
Failure type		–	No break	No break	Complete break

Table 3: Metal coating applications

	Method	Unit	Ancamide® 2842	Ancamide® 910	Ancamide® 2861
Mandrel bending	ISO 6860 and ASTM D522	Elongation in %	> 30	> 30	> 30
Impact direct	ISO 6272 and ASTM G14	kg/cm	> 200	> 200	> 200
Crosshatch	ASTM D3359	scale 1-5; 1 best	1	1	2
Erichsen Cupping	DIN EN ISO 1520:2007 11	cm	–	> 10	8.5

Figure 6: Mandrel bending of formulations based on Ancamide® 2842 (left) and Ancamide® 2861 (right).

bending and Erichsen cupping. An elongation of up to 30 % and 200 kg/cm direct impact were applied which are the upper limits of the methods. No cracking or adhesive failure of the films was observed even in case of the least flexible hardener Ancamide® 2861. In addition, cross-hatch tests were performed which confirmed very good adhesion properties.

CONCLUSION AND OUTLOOK

The market need for flexible epoxy systems which combine high durability and adhesion with improved elongation is addressed by amine hardeners based on established polyamide technology using flexible monomers. This includes two new developments, Ancamide® 2842 and Ancamide® 2861, which add up to Evonik's portfolio of tailor-made epoxy curing agents. The property profile ranges broadly from high strength and fast cure up to very high elongation combined with long pot life and low exothermic curing. This allows formulators to pick the best solution for their specific project and end use. Since the three hardeners are fully compatible with each other, formulation properties can be further adjusted by mixing. For instance, Ancamide® 2842 can be used as a co-amine to lower the formulation viscosity and enhance curing speed when combined with Ancamide® 910.

Target applications include flexible coatings for metal protection of demanding geometries such as T beams or curved elements where cracking of the coating and subsequent metal corrosion have to be avoided. Due to the excellent hardness development and strength of Ancamide® 2861, it can be an ideal choice for flexible floor coatings with high impact resistance. On the other hand, Ancamide® 2842 and Ancamide® 910 offer excellent adhesion and elongation required in demanding 2K adhesive applications.

Due to their polymeric nature, Ancamide® 910 and especially Ancamide® 2861 exhibit excellent EHS profile with beneficial labeling. In addition, all curing agents are partially biobased since fatty acids are used as co-monomers. The fast property and hardness development of systems with Ancamide® 2861 shortens the downtime which further adds to the sustainability benefits. Higher efficiency helps to save energy, while providing a high protection level on metal and concrete surfaces.

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