TECHNICAL INFORMATION

TAILOR-MADE CURING AGENT SOLUTIONS FOR STRUCTURAL EPOXY ADHESIVES

Structural bonding as a joining process has become increasingly important in recent decades. The automotive, aircraft manufacturing and shipbuilding, electronics and construction fields in, particular, have benefited from the technical development of adhesive bonding technology. Lightweight and multi-material designs, progressive integration and miniaturization, as well as, increasing complexity have created a steady rise in technical requirements on components, and thus also on joining processes. In the above applications, structural bonding offers practical advantages over other integral, as well as, frictional and positive joining processes. For example, material composites and composite materials consisting of different materials, such as metals, polymers, glass, ceramics or low-thickness substrates can be realized, which cannot be achieved with other processes or only at a disadvantage. Further advantages of an adhesive bond include homogeneous stress distribution or stress compensation by two-dimensional force transmission, the possibility of compensating component tolerances, and the additional function as a seal and, corrosion protection, as well as, vibration damping. Despite some challenges, such as lower thermal resistance, the issue of de-bonding or instant strength, structural bonding is now an optimum solution for many bonding options and manufacturing processes. In addition to acrylates and urethanes, the leading adhesive technologies in this field are based on epoxides, which are among the most widely used structural adhesives.

Performance characteristics of system types

1c epoxies
- Maximum strength
- Chemicals and thermal resistance

2c acrylates
- Bonding of plastics
- Impact strength
- Fast curing

2c PU
- Fatigue resistance
- Multi-material bonding
- Low cost

SMP
- Elastic
- Gap-filling
- Multi-material bonding
- Not hazardous

◄ **RIGID** BONDING ||||||||||||||||||||||||||||| **ELASTIC** BONDING ►

2c epoxies
- High strength and tenacity
- Chemicals and thermal resistance

1c acrylates
- Very fast setting
- Simple application
- Versatile
- High tenacity

1c PU
- Elastic
- Fast setting
- Multi-material bonding
- Low cost

Silicones
- High thermal resistance
- Elastic
- Gap-filling

AT A GLANCE

- **Epoxy adhesives can be adapted to numerous requirement profiles with regard to processing and curing, and the required final properties of the bond can be adjusted**
- **The curing agent can be used to specifically influence decisive properties of the adhesive**
- **Evonik offers a wide range of high-quality amine-based curing agents and accelerators for structural one-component and two-component epoxy adhesivese**

One-component systems
- Imidazoles, substituted ureas and modified aliphatic amines lower the activation temperature and increase the reactivity of dicyandiamide
- Modified aliphatic amines enable systems for low curing temperatures (>80°C) and high storage stability

Two-component systems
- Curing agent spectrum based on modified and non-modified, cyclic and non-cyclic amines, amidoamines and polyamides
- Depending on the curing agent, rigid to flexible and impact-modified adhesive bonds with good resistance can be realized
- Curing agents are selected to suit the required application curing and final properties, such as curing temperature, gel time and thermal resistance

EVONIK Leading Beyond Chemistry

WHY EPOXY ADHESIVES?

The success of epoxies in structural adhesives is based primarily on their excellent mechanical properties, very good adhesion to a wide range of substrates, and exceptionally good resistance to environmental influences such as moisture, chemicals and temperature. In addition, they shrink only slightly during curing and generally contain no volatile matter. Although epoxies are considered to be rather brittle, this disadvantage can be more than compensated for by a wide range of additives and modification options. Epoxy adhesives can be used as one-component or two-component systems and can be cured in hot conditions or at room temperature, depending on the design. There are variety of possible application forms, such as pastes, films, solids, aqueous dispersions, liquids or solvent-based adhesive systems. This diversity allows adapting epoxy adhesives easily to numerous requirement profiles regarding processing, the curing process and the required final properties of the bond.

Epoxy adhesives essentially consist of an epoxy resin and a curing agent. Usually, the epoxy resins are monomeric or oligomeric, bi- or polyfunctional oxiranes which are mainly derived from bisphenols or polyphenols. The curing agents used are typically nucleophiles, such as mainly bi- or polyfunctional amines, but also thiols or acid anhydrides, which crosslink with the epoxy resin to form highly branched thermoset plastics in a polyaddition reaction. Catalysts such as tertiary amines, imidazoles or certain Lewis acids are also important for initiating the homopolymerization of the epoxy resin.

Due to the generally high degree of crosslinking, epoxy adhesives exhibit very high mechanical strength values and excellent resistance to environmental. However, they tend to be somewhat brittle, which restricts their use in applications that require, in particular, high peel and impact strengths as well as stability under dynamic stress. In this context, the degree of crosslinking is an important factor, and can be effectively controlled by selecting the proper epoxy resin and curing agent as well as by the curing conditions. Adding further additives, especially impact modifiers or flexibilizers, as well as, anchoring agents and fillers, allows formulating structural adhesives that are capable of bonding a large number of substrates with one another and at the same time can withstand the highest stresses such as high dynamic loads, high stress peaks and many environmental influences over the entire service life of the product.

ADVANTAGES OF EPOXY ADHESIVES

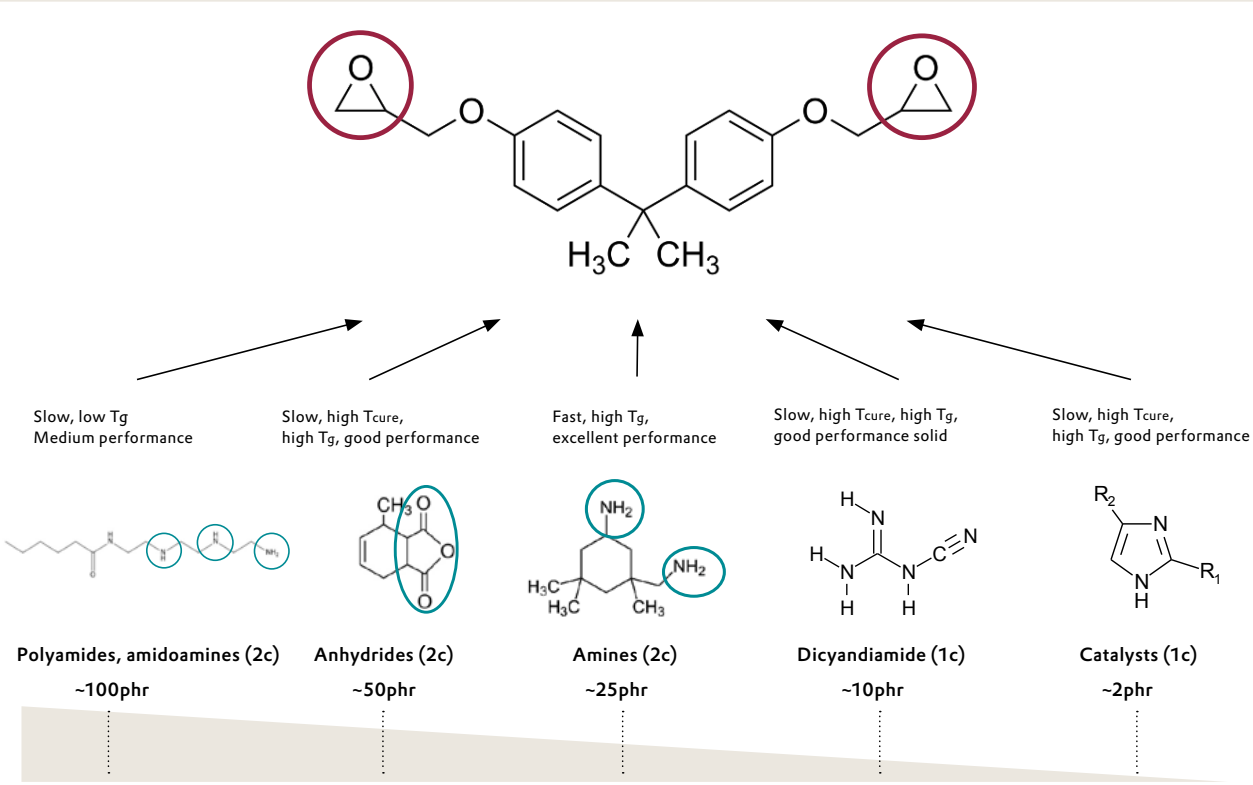
- **Mechanical properties**
- **Good adhesion to various substrates**
- **Resistance to environmental influences**
- **Compatible with one-component and two-component systems**
- **Flexible curing temperature**
- **Suitable for many application forms**

WHAT ROLE DOES THE CURING AGENT PLAY?

The curing agent component, which can be used to specifically influence crucial properties of the adhesive, is one of the most important components in epoxy adhesives. Thus, parameters such as application form, mixing ratio, viscosity, processing time, curing temperature and curing rate can be set to suit the application. Selecting a suitable curing agent is also crucial with regard to the required final properties of the adhesive, such as mechanical strength, flexibility and impact strength as well as thermal and chemical resistance.

EVONIK - SPECIALIST IN THE FIELD OF AMINE-BASED EPOXY CURING AGENTS

In adhesives, Evonik, as global leader in specialty chemicals, has a comprehensive portfolio of products based on various chemical platforms that help adhesive formulators optimize their products in terms of performance, efficiency and sustainability and drive product innovations. In addition to performance modifiers and additives for adhesives, Evonik also offers a wide range of high-quality amine-based curing agents and accelerators for structural epoxy adhesives. These are grouped in the Epoxy Curing Agents product line. The brands Ancamine®, Ancamide®, Amicure® and Dicyanex® as well as Curezol® and Imicure® cover almost the entire range of current amine curing technologies for structural one-component and two-component epoxy adhesives. This range includes not only aliphatic and cycloaliphatic amines, but also polyamides and amidoamines as well as imidazoles and dicyandiamide. **Figure 1** presents an overview of the different amine curing technologies, including a simple property profile, typical application rates and product examples.



Examples of ECA products

Ancamide® 3030	**Only catalysts:**	**Ancamine® 1769**	**Amicure® CG-1200G**	**Curezol® 2MZ Azine**
Ancamide® 500	**Ancamine® 2014AS/FG**	**Ancamine® 2914UF**	**Amicure® CG-1400F**	**Imicure® EMI-24**
	Ancamine® 2441		**Dicyanex 1400B**	

Figure 1: Overview of Evonik amine curing technologies for structural epoxy adhesives, their property profiles, typical application rates and product examples.

APPLICATIONS FOR STRUCTURAL EPOXY ADHESIVES

The range of applications for curing agent technologies thus covers all areas relevant to adhesive technology in which structural epoxy adhesives are used, in particular the automotive and transport fields, product manufacturing, electronics and aerospace applications. **Figure 2** provides an overview of the different areas of application, typical application forms and suitable curing agent technologies.

WHAT ARE THE CURRENT TRENDS?

As the technology leader in amine synthesis and modification and in curing agent formulation, Evonik has an in-depth understanding of current market requirements, customer needs and current trends. In close dialog with its customers, Evonik is able to provide customized solutions to current challenges and new product developments. In the field of structural epoxy adhesives, three main topics that are crucial for future product developments can be mentioned as examples. When it comes to increasing the performance of adhesives, particularly regarding thermal and chemical resistance, as well as, improved impact strength, application-related aspects such as improved bondability of different materials play an important role. On the other hand, sustainability and cost-effectiveness are of critical importance. The focus here is on aspects such as reduction of energy consumption in bonding processes, recycling, regulatory adjustments and an increase in the efficiency of production processes.

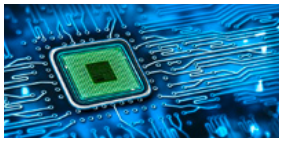
Automotive & Transport	Product manufacture	Electronics	Aerospace
			
APPLICATION			
1c/2c adhesives • OEM applications • Accessories market	**2c adhesives** • Wind energy • Industrial manufacture • DIY applications	**1c/2c adhesives** • Printed circuit boards • Batteries • Potting and encapsulating	**1c/2c adhesives** • Interior trim • Aircraft structures
CURING AGENT TECHNOLOGY			
• Dicyandiamide • Urones • Imidazoles • (Modified) amines • Polyamides • Reaction diluent	• Polyamides • Amidoamines • (Cyclo-)aliphatic amines • Phenolic tertiary amines • Reaction diluent	• Dicyandiamide • (Cyclo-)aliphatic amines • (Modified) amines • Urones • Imidazoles • Reaction diluent	• Aliphatic amines • Dicyandiamide • (Modified) amines • Urones • Imidazoles • Reaction diluent

Figure 2: Overview of fields of application, typical application forms and amine curing technologies.

DURABILITY

- Outstanding bonding properties
- Improved chemical and thermal stability and impact strength

APPLICATION

- Substitution konventioneller Fügetechniken
- Fügen unterschiedlicher Materialien

SUSTAINABILITY

- Adaptation to more stringent regulatory provisions
- Reduction of volatile matter

BIO-BASED RAW MATERIALS

- Reduction of energy consumption in bonding processes
- Recycling capability (De-bonding on demand)

EFFICIENCY

- Improved productivity, shorter cycle times
- Lower curing temperatures
- Multifunctional adhesives → less material is used

Figure 3: Overview of current trends in structural epoxy adhesives.

WHICH IS THE RIGHT CURING AGENT?

Evonik's product portfolio of amine-based curing agents for structural epoxy adhesives can be subdivided in terms of application form, i.e. curing agents for one-component and two-component adhesives. Within this subdivision, further distinctions are made according to additional application-specific properties and requirements for the final properties, which makes selecting the right curing agent much easier.

AMINE CURING AGENT AND ACCELERATOR FOR STRUCTURAL ONE-COMPONENT EPOXY ADHESIVES

One-component structural epoxy adhesives are formulated in such a way that the curing agent and resin components are already mixed in a single container, so mixing during application of the adhesive is no longer necessary. Storage stability is usually between a few days and several months and is determined by the low reactivity or poor solubility of the curing agent at room temperature. More reactive adhesives are also stored at low temperatures to improve storage stability. Curing takes place at higher temperatures of up to 200°C, so such systems can be processed over a long period of time or can be left open before the substrates are joined. This produces adhesive bonds with very good adhesion, even on oiled surfaces, which have excellent mechanical strength, as well as, high moisture, chemical and thermal resistance.

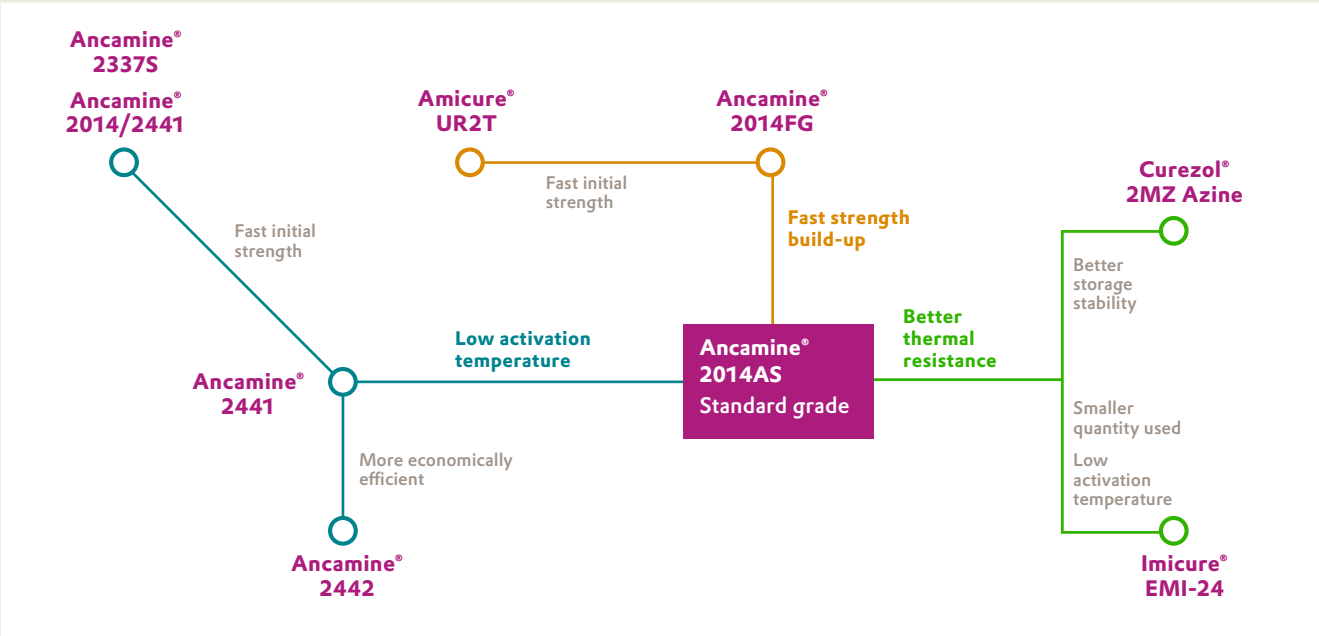
Flexibilization and impact modification can be easily achieved by means of additives and performance modifiers.

In addition to dicyandiamide which is the dominant curing agent in this field, the Evonik product portfolio for one-component epoxy adhesives includes a range of modified aliphatic amines, imidazoles and substituted ureas that can be used as accelerators for dicyandiamide and significantly improve the reactivity and activation temperature of the system. Especially the modified aliphatic amines reduce the activation temperature significantly while offering long storage stability. In this way, the use of **Ancamine® 2014 AS/FG,** as well as, **Ancamine® 2441** and **2442**, especially in combination with **Ancamine® 2337S**, allows achieving acceptable curing times from 120°C onwards. At higher temperatures, high initial strengths with very short curing times of less than one minute are possible in combination with **Ancamine® 2337S**, making the modified aliphatic amines also suitable for induction curing. **Table 1** shows an overview of the available curing agents and the corresponding decision aid („Tube Map") is shown in **Scheme 1**.

Table 1: Accelerators for dicyanamide-based structural one-component epoxy adhesives

Curing agent	Type	Melting range [°C]	Application rate* [PHR]	$T_{ACTIVATION}$ [°C]	Storage stability (42°C) [M]	T_g (max) [°C]
Amicure® CG-1200G	Dicyandiamide	207 - 212	4 - 15	180	>3	140
Ancamine® 2337S	Mod. aliphat. amine	63 - 78	10**	100	>1	130
Ancamine® 2014AS	Mod. aliphat. amine	98 - 106	5	125	>3	135
Ancamine® 2014FG	Mod. aliphat. amine	98 - 106	5	125	>1	135
Ancamine® 2442	Mod. aliphat. amine	~112	5	110	>3	135
Ancamine® 2441	Mod. aliphat. amine	124 - 135	5	110	>3	135
Imicure® EMI-24	Semi-solid imidazole	~35	0.5 - 5	125	>9 h	155
Curezol® 2MZ Azine	Solid imidazole	247 - 251	6 - 8	145	<45 d	155
Amicure® UR2T	Subst. urea	182 - 190	0.5 - 3	140	<7 d	135

*) with 6 PHR Amicure CG-1200G **) + 4 PHR Ancamine 2014 AS/FG or 2441/2442



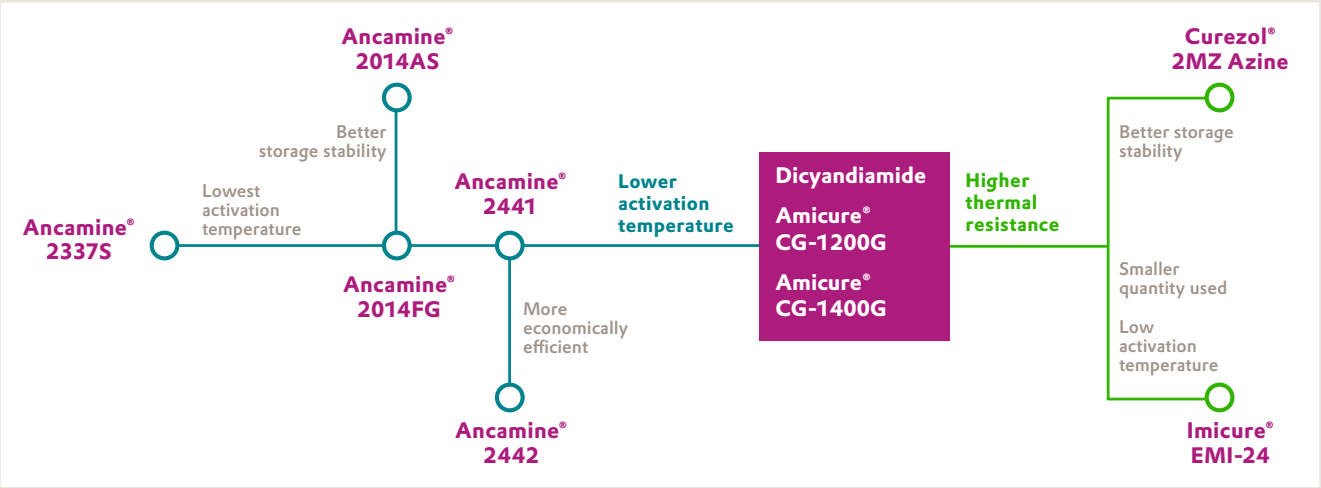
Scheme 1: Tube map for accelerators for dicyanamide-based structural one-component epoxy adhesives.

Some of the curing agents mentioned above, especially the modified aliphatic amines, can also be used as sole curing agents for one-component systems, especially when very fast curing or curing at low temperatures <100°C is required and long storage stability, even at higher storage temperatures, is a crucial factor. **Ancamine® 2337S** allows curing even from 80°C with acceptable curing times. Higher thermal stabilities >100°C can be achieved with **Ancamine® 2441** and **2442** , starting at curing temperatures as low as 100°C. The thermal stability >150°C can be further improved by using the imidazoles **Imicure® EMI-24** and **Curezol® 2MZ** Azine, but this in turn requires higher curing temperatures. The corresponding curing agents as well as the associated "Tube Map" are listed in **Table 2** and **Scheme 2**.

Table 2: Curing agents for structural one-component epoxy adhesives.

Curing agent	Type	Melting range [°C]	Application rate* [PHR]	TActivation [°C]	Storage stability (42°C) [M]	T_g (max) [°C]
Amicure® CG-1200G	Dicyandiamide	207 - 212	4 - 15	180	>3	140
Ancamine® 2337S	Mod. aliphat. amine	63 - 78	45	70	>1	70/85 (60 PHR)
Ancamine® 2014AS	Mod. aliphat. amine	98 - 106	25 - 30	75	>3	110
Ancamine® 2014FG	Mod. aliphat. amine	98 - 106	25 - 30	75	>1	110
Ancamine® 2442	Mod. aliphat. amine	~112	20	93	>3	115
Ancamine® 2441	Mod. aliphat. amine	124 - 135	20	100	>3	115
Imicure® EMI-24	Semi-solid imidazole	~35	1 - 4	95	>5 h	160
Curezol® 2MZ Azine	Solid imidazole	247 - 251	6 - 8	145	<20 d	156

*) with 6 PHR Amicure CG-1200G **) + 4 PHR Ancamine 2014 AS/FG or 2441/2442



Scheme 2: Tube map for curing agents for structural one-component epoxy adhesives.

AMINE CURING AGENTS AND ACCELERATORS FOR STRUCTURAL TWO-COMPONENT EPOXY ADHESIVES

Two-component structural epoxy adhesives are formulated so that the curing agent and resin components are separate from each other in individual containers, which allows high storage stability. The curing reaction is initiated by mixing the components before application and takes place even at room temperature so that such systems can be processed only for a limited time before the substrates are joined. Depending on the curing agent, two-component systems produce rigid to flexible and impact-modified adhesive bonds which exhibit good resistance to environmental influences such as moisture, chemicals and temperature.

To achieve the final properties, in particular higher thermal resistance, systems curing at room temperature should also be subjected to hot curing. Higher temperatures also enable accelerating the curing reaction.

With the **Ancamine®** and **Ancamide®** product lines, the Evonik product portfolio for two-component epoxy adhesives includes a broad selection of different curing agents from the range of modified and non-modified, cyclic and non-cyclic amines, amidoamines and polyamides. **Ancamide® 3030**, a polyamide with medium gel time and good all-round properties, is the standard product in this field and suitable for a wide range of applications.

Table 3: Curing agents for structural two-component epoxy adhesives with long gel times.

Curing agent	Type	Curing condition	Viscosity (25°C) [mPa.s]	Application rate [PHR]	Gel time [min]	T_g after 7d RT [°C]
Ancamine® 2927	Amine	Heat	100 - 200	15	>800	65 (2h @75°C)
Ancamide® 3419	Amidoamine	RT/heat	50 - 160	75	520	55 (2h @80°C)
Ancamine® 2919	Amine	Heat	5-15	24	500	110 (T_g max.)
Ancamide® 506	Amidoamine	RT/heat	200 - 500	50	400	60
Ancamide® 500	Amidoamines	RT/heat	200 - 450	50	180	50
Ancamide® 910	Polyamides	RT	6,000	110 - 125	120	25
Ancamide® 3030	Polyamides	RT	300 – 600@75°C	50	80 - 140	57
Ancamide® 261A	Polyamides	RT/heat	30,000 – 50,000	65	75	50

If longer gel times are required, **Ancamine® 2919** and **Ancamine® 2927** offer significantly longer gel times of up to 800 minutes; these products, however, require curing at higher temperatures to achieve the final properties. **Table 3** (see previous page) gives an overview of further curing agents, sorted by decreasing gel time.

Ancamine® 1769 and **Ancamine® 2914UF** provide higher reactivities for two-component structural epoxy adhesives requiring short curing times at room temperature and reduce the gel time to 8 minutes. **Table 4** shows an overview of the curing agents with short gel times at room temperature. If, on the other hand, high thermal resistance is required and curing at higher temperatures is tolerable, curing agents based on polycycloaliphatic amines such as **Ancamine® 2167** and **Ancamine® 2264** deliver excellent performance. The properties of the relevant products are summarized in **Table 5**. **Scheme 3** on the next page provides an additional guide for selecting the right curing agent to achieve the required target properties of the adhesive with regard to application and final properties.

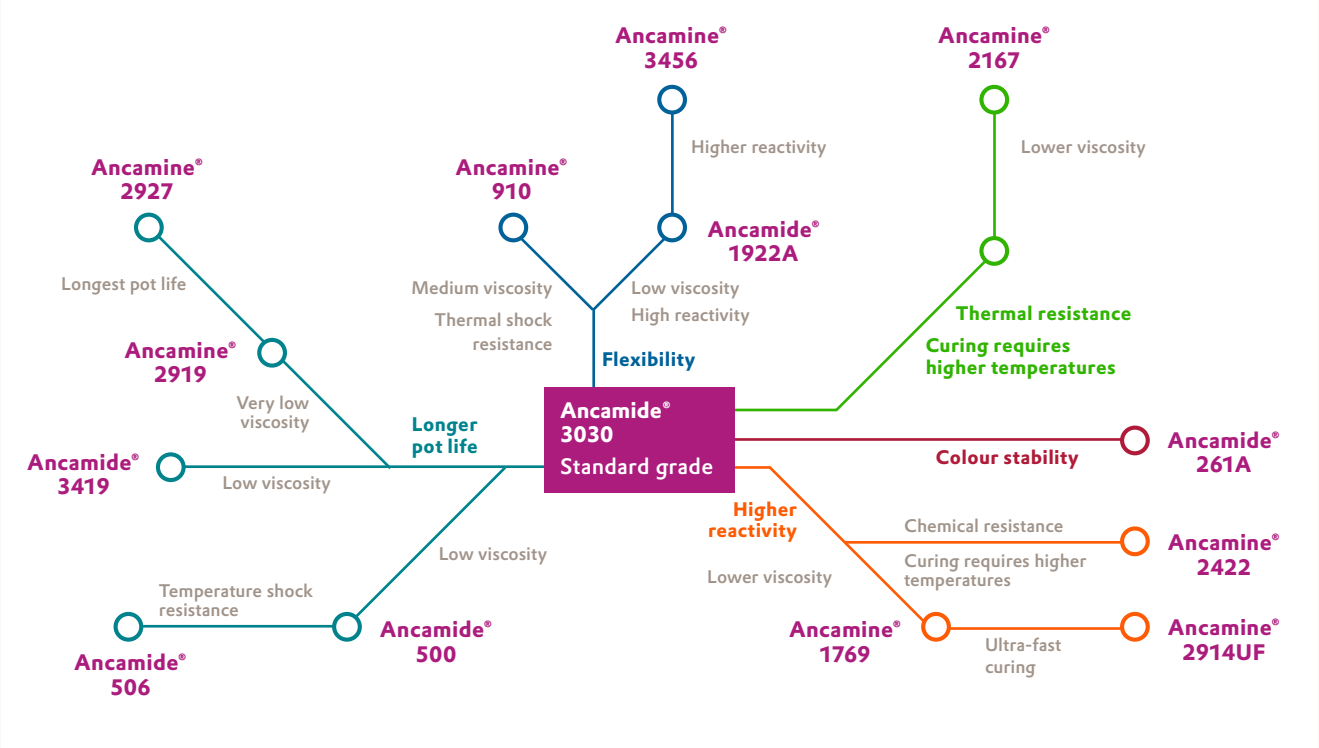
Evonik's Epoxy Curing Agents product line thus offers a comprehensive range of amine-based curing agents, based on various chemical platforms, and thus covers almost all adhesive-relevant application areas for one- and two-component structural epoxy adhesives. Evonik thus offers adhesive formulators a wide range of options for tailoring their systems to a wide variety of requirement profiles. In addition, Evonik supports its customers in selecting the right curing agents and in overcoming challenges in the development of new structural epoxy adhesives.

Table 4: Fast curing agents for structural two-component epoxy adhesives.

Curing agent	Type	Curing condition	Viscosity (25°C) [mPa.s]	Application rate [PHR]	Gel time [min]	T_g after 7d RT [°C]
Ancamine® 2914UF	Modified amine	RT	300 – 2,000	50	8	50
Ancamine® 1769	Modified amine	RT/heat	600 – 900	25	24	99 (2h 100°C)
Ancamine® 2422	Aliphatic amine	RT/heat	1,500 - 2,500	26	15 (Novolak)	-
Ancamine® 3456	Mod. aliphat. amine	RT	500 – 1,500	125 – 135	35	-
Ancamine® 1922A	Aliphatic amine	RT/heat	10	29	60	47

Table 5: Curing agents for structural two-component epoxy adhesives with high thermal resistance.

Curing agent	Type	Curing condition	Viscosity (25°C) [mPa.s]	Application rate [PHR]	Gel time [min]	T_g after 7d RT [°C]
Ancamine® 2167	Polycyclo-aliphat. amine	Heat	210	30	210	161
Ancamine® 2264	Polycyclo-aliphat. amine	Heat	2,600	30	195	164



Scheme 3: Tube map for curing agents for structural two-component epoxy adhesives.

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