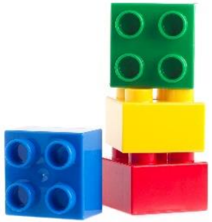
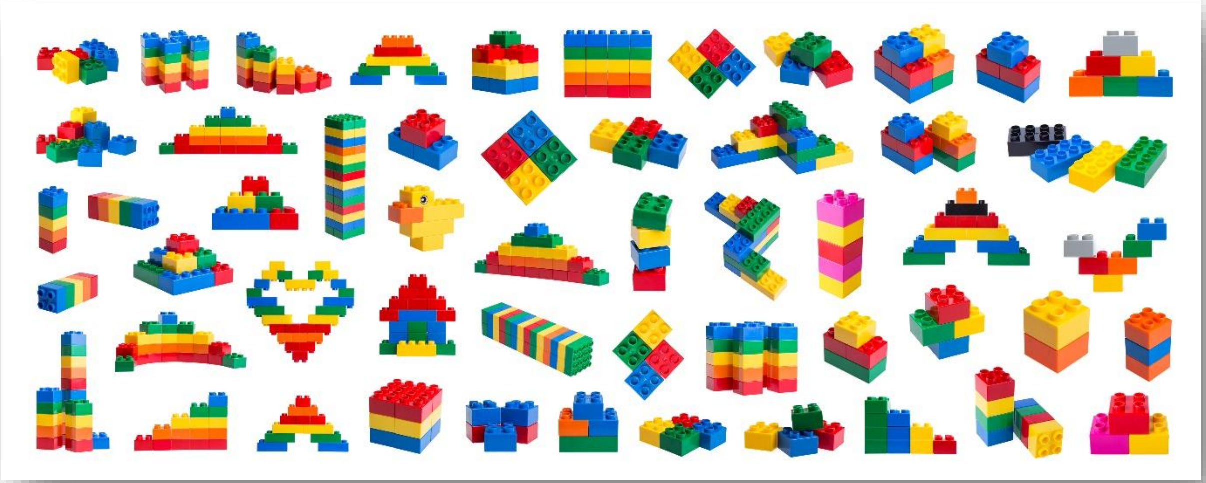
Manufacturers of low-volume customised polymers at the end of the supply chain

Examples to illustrate the problem

Many customised polymers are produced with just a few building blocks





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Reactive polyurethane hot melts (PURHM) in the scope of PRR

PURHM – tool box for customised precursors

- The adhesive industry manufactures PURHM from the chemical reaction of a limited number of diisocyanates and polyols
- The most common diisocyanate is MDI, for special products IPDI and a few low MDI-monomer intermediates with Mn<1500 dalton (manufactured in-house and 3rd party) are used
- Di- and trifunctional polyols are based on polyethers (propylenglycols & combinations with ethylenoxide) and polyesters (amorphous, crystalline) at molecular weights 400 – 5000 dalton
- Polyesters are formulated (in-house and 3rd party) from multiple di-/tri-carboxylic acids of different nature (aromatic and aliphatic)and di-/tri-ols

A limited number of monomeric and polymeric raw materials are sufficient to develop infinite number of individual polymer precusors used as reactive PU hot melt adhesives

Reason for customisation of PURHM

Composition of PURHM varies to address specific processing and performance requirements of very different application areas, e.g.

- Improving efficiency in production, e.g. faster line speed in assembly operations
- Lower application temperatures to reduce energy consumption
- New substrate combinations including recycled & bio-based materials
- New design of the assembled part, e.g. lightweight, design for recycling
- More demanding properties in end use
- …

supporting the Green Deal initiative of the European Commission and UN SDGs

Customisation and continous improvement of PURHMs is key to help our customers to stay competitive and respond to changing market requirements

PURHM supplier landscape

- **The adhesives industry is mainly structured around SMEs** plus a few multinational operating companies
- In-house polymerisation of PURHM is common across the adhesives industry to meet the **demand for tailor-made products in a timely manner** across multiple application areas
- **About 1,400* different PURHM polymer precursors** with molecular weight number average <10,000 da
  (Survey of German manufacturers)

14%	<1 tons/a
29%	1- 10 tons/a
37%	10-100 tons/a
20%	100-1000 tons/a
<1%	>1000 tons/a

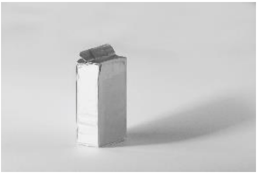
- **Each individual PURHM polymer precusor is almost exclusive from one supplier**

*IVK (German adhesives association) survey on number of individual polymer products and assignment to tonnage bands, July 2020

Innovation in a dynamic market is key for SMEs and larger adhesive suppliers to stay competitive

PURHM application areas & markets

- PURHM are used for assembly with applications across multiple markets, e.g.
  - Graphic arts
  - Wood & furniture industry
  - Textile lamination
  - Rigid packaging
  - Electronics
  - White goods
  - Automotive OEM & Tier1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- **Customers are mainly SMEs** plus multinationals
- Life cycle of the finished good influences the **life cycle of the PURHM polymer,** which can be **as short as <3 years, depending on the market**
- All PURHM are cured after assembly with air humidity to convert them into high molecular weight polyurethanes

PUR Lamination Adhesives

PUR Lamination Adhesives

- Lamination adhesives are similar in chemistry to PURHM covered by previous example but are used in different sectors.
- Main use for such products is to hold together different films, that can be of different nature (different plastic films, like PP, PE, PET, etc., paper and plastic, aluminium and plastic and so on).
- They are determinant for the final properties of manufactured articles, as the structures must grant resistance to various agents.

PUR Lamination Adhesives

- PUR Lamination adhesives derive from a chemical reaction between diisocyanates and polyesters or polyols (in some cases a mixture of the two).
- Most common diisocyanate is MDI, for special products HDI, IPDI, TDI and some low MDI-monomer intermediates with Mn <1500 Dalton (manufactured in-house or bought outside) are used.
- Di- and Trifunctional hydroxylic moieties are based on Polyesters (amorphous or crystalline), Polyethers (propylenglycols & combinations with ethylenoxide) with molecular weights in the range 400 – 5000 Dalton
- Polyesters are formulated (in-house and 3rd party) from multiple di-/tri-carboxylic acids of different nature (aromatic and aliphatic) and di-/tri-ols, so can be linear or branched

PUR Lamination Adhesives

- Starting polyesters or polyols may be of different nature, in order to give flexibility to the adhesive if the final article needs to be bent or to resist to such sollecitations, or may give resistance to other foreseeable conditions to which final film will be exposed.
- So, many kinds of polyesters are used as starting materials for such adhesives.
- They are then reacted in house with diisocyanate monomers, oligomers and polymers in order to manufacture the final adhesive. As also those chemicals are very numerous, and there are a lot of possible combinations (a factorial calculation shows how big the number of possible combinations could be), the number of possible registrations for a single company, even if belonging to SMEs, is huge. A rough evaluation can of the number of such products tells us that total number is in the range of thousands.
- Therefore, a wider approach to the grouping concept is needed.

PUR Lamination Adhesives

- Final applications include food packaging, industrial applications and packaging as well as some applications for professional use.
- Many packagings are multimaterial, but also if the market will go in direction of monomaterials, adhesives will still be required.

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PUR Lamination Adhesives

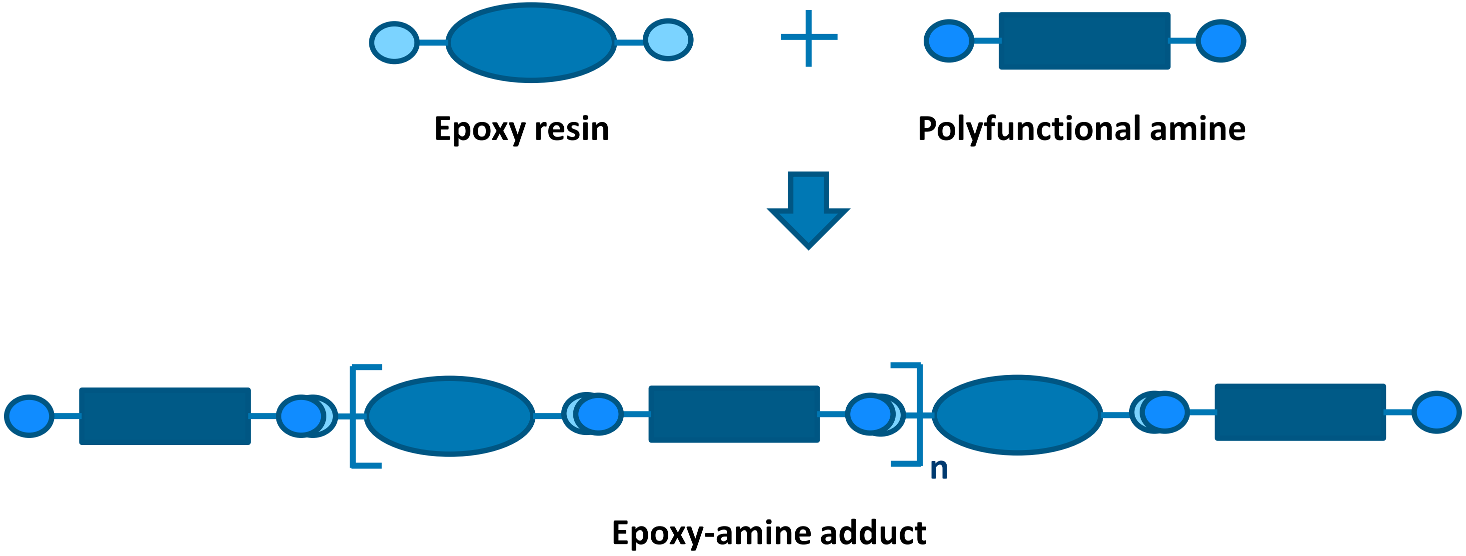
- Situation is furthermore complicated by the fact that such adhesives may be used as single component ones (for relatively high molecular weight ones, which will use as curing agent air humidity) or as two components ones, case in which there is a further reaction with an hydroxyl terminated curative.
- In both cases it should be kept in mind that by this reaction a new further polymer is produced by curing, and such polymer is produced in situ on the application machine of the converter, and thus it must be considered as exempt or have a different evaluation in confrontation with the marketed polymers.

Polymeric Epoxy-Amine Adducts in the Scope of PRR

EPNHA – Tool Box for Customised Precursors

- Epoxy-amine adducts (EPNHA) are used as customised precursors in many tailor-made epoxy products, such as adhesives, coatings, and construction materials
- They are produced by reacting epoxy resin with di- or polyfunctional amines (see next slide)
- They can be both polymeric or non-polymeric – depending on the process
- Epoxy resin is most commonly used as epoxy component
- A large variety of amines is used for adducts, ranging from aliphatic, cycloaliphatic to aromatic-aliphatic with two or more amino groups
- More than one amine can be used which results in a large number of EPNHA
- Molecular weights tend to be low (< 5,000 Da)

EPNHA – Reacting Epoxy with Amine



Large Variety of EPNHA

- The table shows an example of possible EPNHA when using **two amines**:

	Amine 1	Amine 2	Amine 3	Amine 4	Amine 5	…
_	**Adduct 1**	**Adduct 2**	**Adduct 3**	**Adduct 4**	**Adduct 5**	…
Amine 2	Adduct 1-2	_	Adduct 3-2	Adduct 4-2	Adduct 5-2	…
Amine 3	Adduct 1-3	_	_	Adduct 4-3	Adduct 5-3	…
…	…	…	…	…	…	…

- A large number of adducts are possible.
- More than 100 amines are available commercially that can be used for EPNHA.
- Approx. 15 - 20 amines are commonly used.

Large variety of epoxy-amine adducts is possible.

Customised EPNHA

Customised EPNHA allow the formulation of tailor-made epoxy products, e.g. to

- Improve application properties
- Respond to specific customer demands
- Adjust curing speed/pot-life
- Improve durability and lifespan
- Improve efficiency in production, e.g. faster line speed in assembly operations
- Reduce the product's hazard profile

Customisation and continous improvement of EPNHA is key to stay competitive and flexible in changing market environments.

EPNHA Landscape

- Epoxy-amine adducts are commercially available from several medium to large raw material suppliers
- A large number of SME coatings, adhesive and construction chemical manufacturers produce their own epoxy-amine adducts – often in addition to buying from raw material suppliers
- Reasons for SMEs to produce their own epoxy-amine adducts are customisation of their products and/or cost savings

1- 10 tons/a	Specialty products
10-100 tons/a	Standard range/specialties
100-1000 tons/a	Standard range
>1000 tons/a	Commodities

Innovation in a dynamic market is key for SMEs and larger suppliers to stay competitive

EPNHA Application Areas & Markets

- Epoxy-amine adducts are used in reactive, 2-part epoxy products, such as
  - Adhesives
    - Industrial (e.g. wind turbines)
    - Construction (concrete and steel structures)
    - Automotive
  - Coatings
    - Corrosion protection
    - Marine coatings
    - Heavy duty coatings
  - Construction chemicals
    - Injection materials (reinforcing cracks in concrete)
    - Tile adhesives
    - Flooring (e.g. industrial facilities/warehouses/car parks)
- Epoxy products cure after application to form crosslinked high molecular weight resins

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EPNHA Conclusions

- The resulting EPNHA no longer carry epoxy groups – instead they are amine end-capped
- The hazards profile is reduced compared to monomeric amines
- Due to combinations of amines a large variety of adducts is possible
- Backbone and end group structures are very similar for EPNHA
- Structural features and hazard profile of comparable adducts tend to be very similar – which should facilitate grouping
- Grouping could reduce the potentially large number of registrations
- Former downstream users will become registrants for EPNHAs

Grouping approaches for EPNHA will reduce the burden for SMEs to reduce large number of adducts