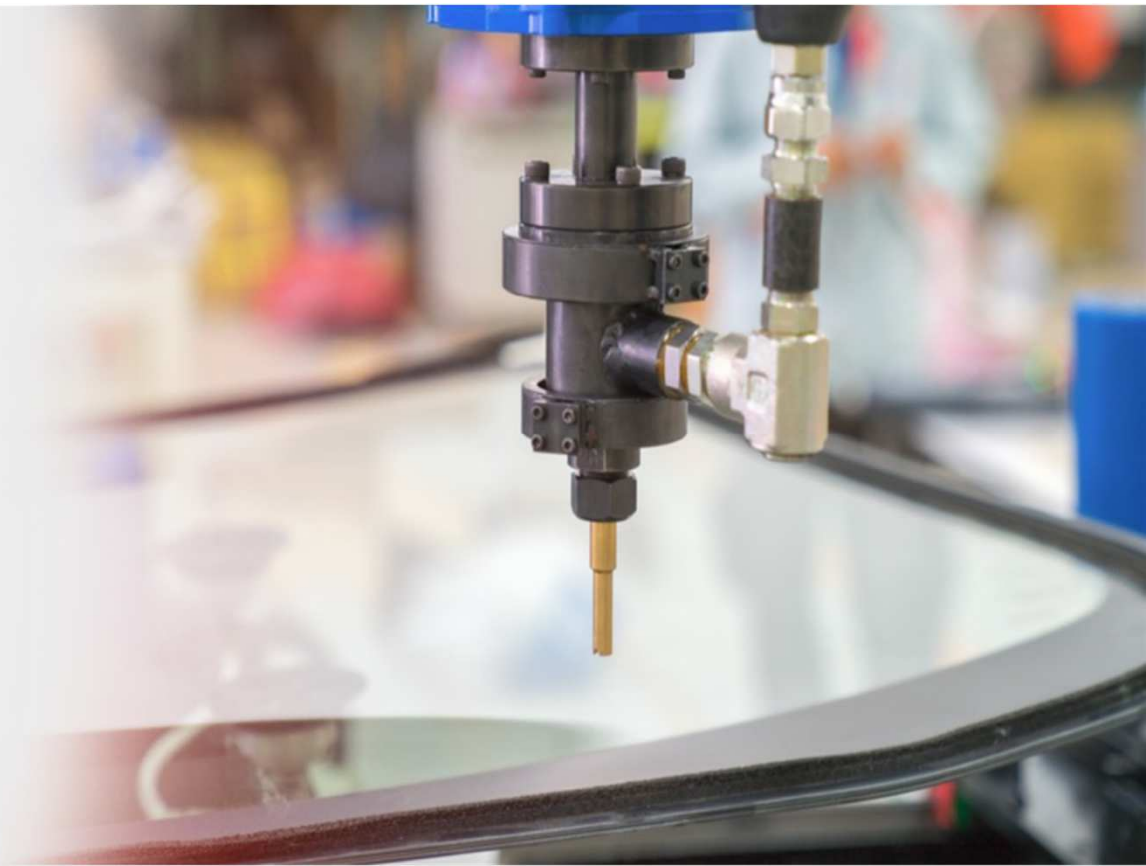


# Advancements in low free (LF) isocyanate prepolymer design for reactive adhesive systems

# Agenda

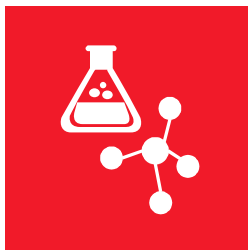
1. About LANXESS Urethane Systems
2. Chemistry of Low Free (LF) Isocyanate Polyurethanes
3. Customized LF Prepolymers as Platform for Low Monomer Hot Melts



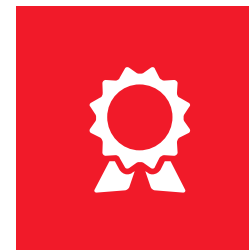
# LANXESS Urethane Systems is part of a global specialty chemicals company



Technology leader in Low Free (LF)\* isocyanate technology



>60 years of experience in urethane chemistry



A leading supplier of cast urethane systems globally



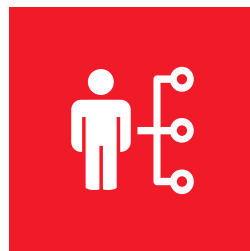
6 production plants globally



7 application development centers globally



1 world-class R&D center in the USA



>500 products to serve customers' needs

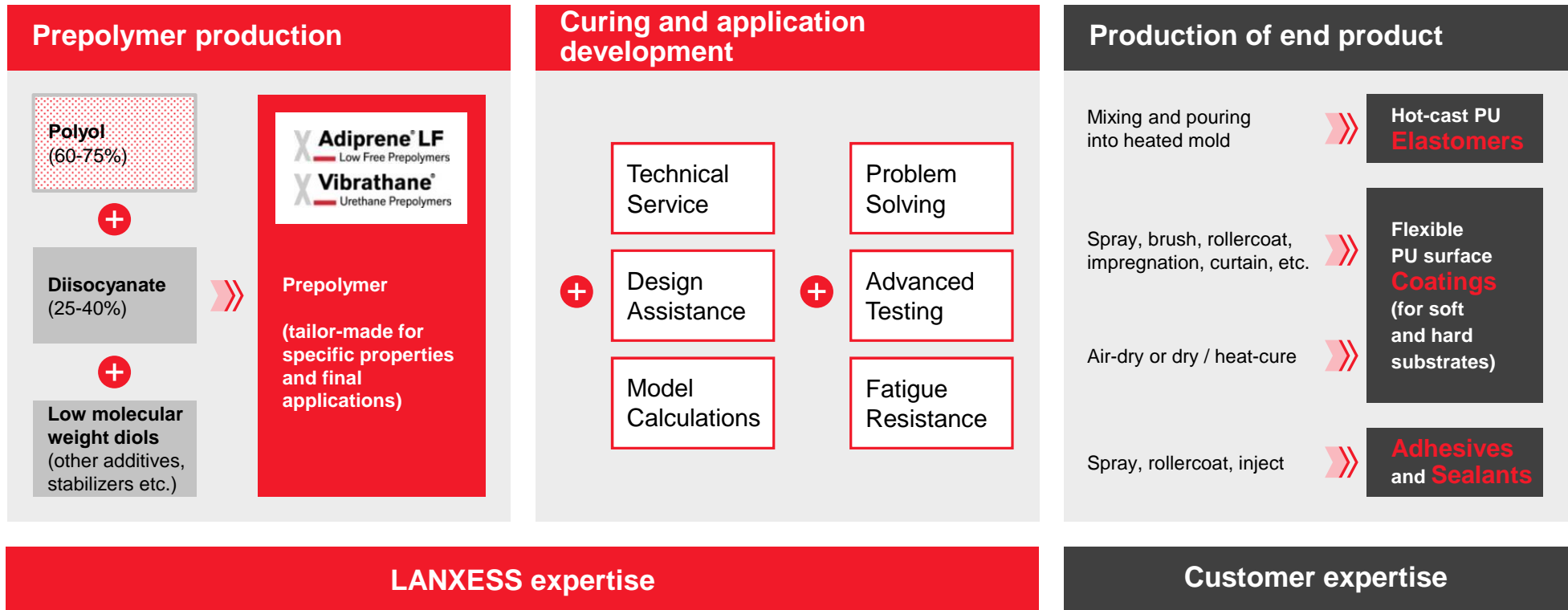


>250 m€ sales in >60 countries



~400 employees globally

# A world leader in specialized systems for urethane elastomers, coatings, adhesives and sealants



Part of LXS / Urethane Systems value creation
  Sourced raw materials / intermediates
  End products

# LANXESS Urethane Systems offers materials for a very diverse set of applications



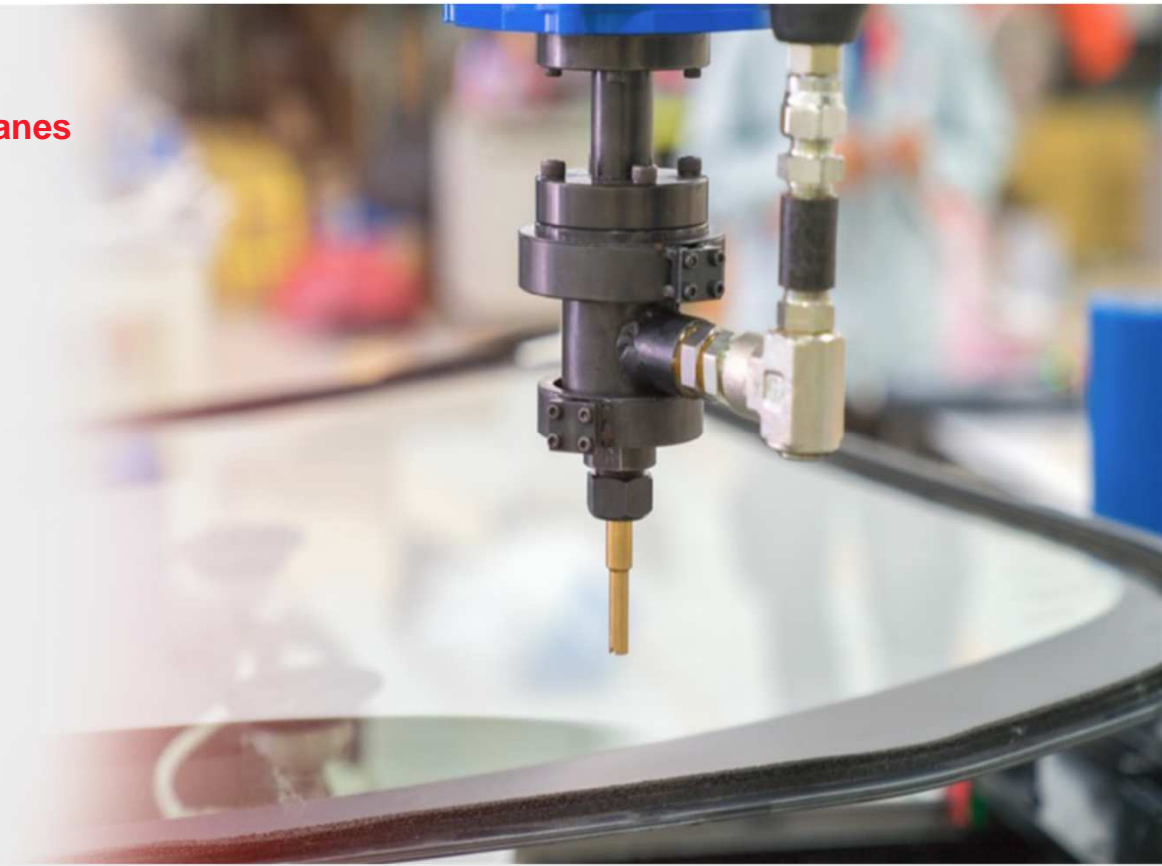
**Thickness**  
100 mm

<b>Wheels</b> 	<b>Mining</b> 	<b>Subsea Oil &amp; Gas</b> 	<b>Oil Pipelining</b> 	<b>Cosmetics</b> 	<b>Agriculture</b> 	<b>Infrastructure</b> 
<b>Machinery</b> 	<b>Military</b> 	<b>Seals</b> 	<b>Paper</b> 	<b>Food</b> 	<b>Belts</b> 	<b>Concrete Molds</b> 
<b>Electronics</b> 	<b>Sports Track</b> 	<b>Abrasives</b> 	<b>Carpet Underlay</b> 	<b>Medical</b> 	<b>Fabric Belts</b> 	<b>Ballistics</b> 
<b>Sealants</b> 	<b>Textiles</b> 	<b>Coil Coatings</b> 	<b>Adhesives</b> 	<b>Construction</b> 	<b>Automotive</b> 	<b>Metal Protection</b> 

<0,1 mm

# Agenda

1. About LANXESS Urethane Systems
- 2. Chemistry of Low Free (LF) Isocyanate Polyurethanes**
3. Customized LF Prepolymers as Platform for Low Monomer Hot Melts



# Upcoming isocyanate restriction, and OEM push for lower free monomer A&S products

## ECHA's draft for the restricted use of free isocyanates

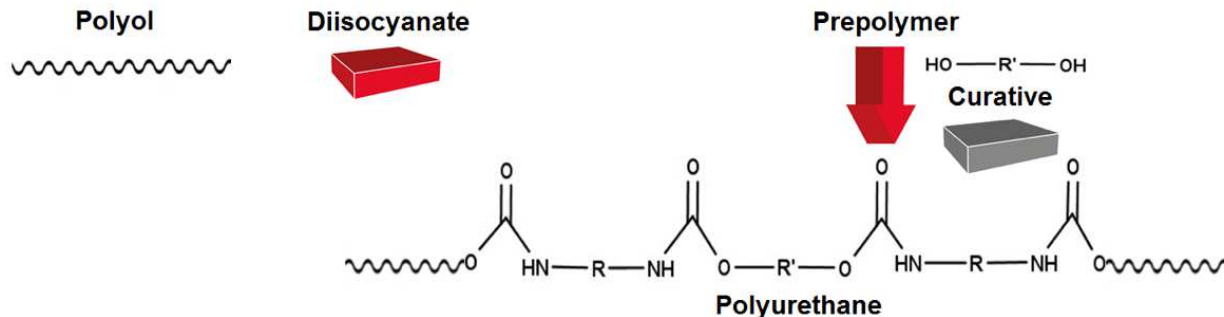
- Products containing **monomeric diisocyanates at levels of 0.1 wt% and above** will be restricted in industrial and professional applications
- They can be used only after **implementation of technical and organizational measures** as well as a minimum **standardized training of the user**
- **Exempted** are products
  - with **monomeric diisocyanate content <0.1 wt%** or
  - where a **very low potential risk** can be shown



The use of low free monomer prepolymers (<0.1%) would avoid any impact of the restriction

# Most reactive PU adhesives are built from prepolymers with residual isocyanate that needs to be removed

## Prepolymer Synthesis Process and benefits of its use



### Safety

- No handling of raw isocyanates
- Improved industrial hygiene

### Quality

- Delivers consistent and reliable elastomers and adhesives
- Achieves tight control of viscosity for processing consistency

### Performance

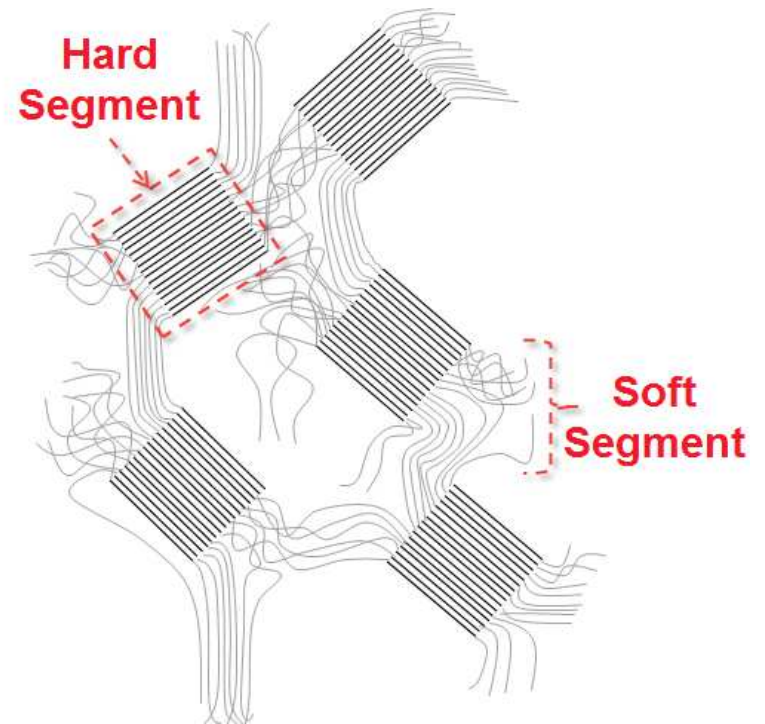
- Drives controlled morphology for enhanced phase segregation
- Allows functional groups to be added to the backbone



# Prepolymers enable unique adhesive formulations designed for target applications

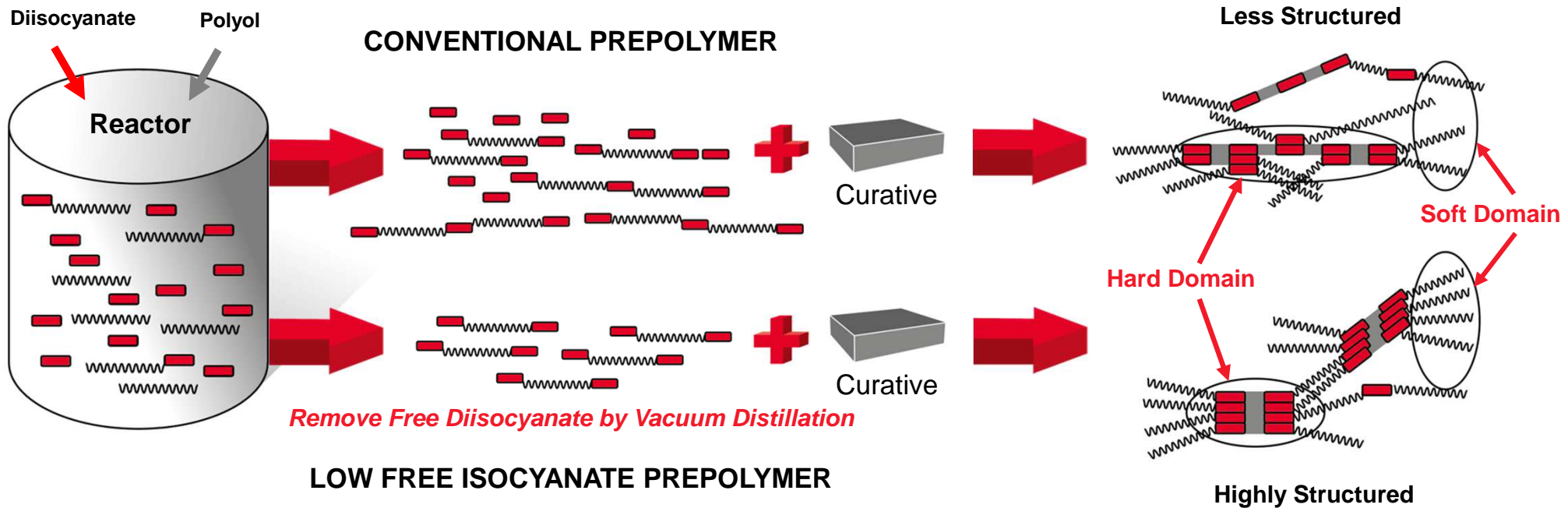
## Prepolymers enable enhanced adhesive performance

- **Structure-property relationships** in PU adhesives are governed by phase segregation morphology between hard and soft segments and molecular architecture
- **Prepolymer** approach drives **controlled morphology** and achieves **enhanced phase segregation** of the hard and soft segment domains enabling the creation of **high performance** materials
- The phase separation morphology is driven by the degree of order within the hard segment (rigid domain) that is governed by:
  - Isocyanate chemical structure and concentration
  - Chemistry and concentration of chain extender
  - Chemistry and molecular weight of the polyol
  - Secondary intermolecular forces such as hydrogen bonding

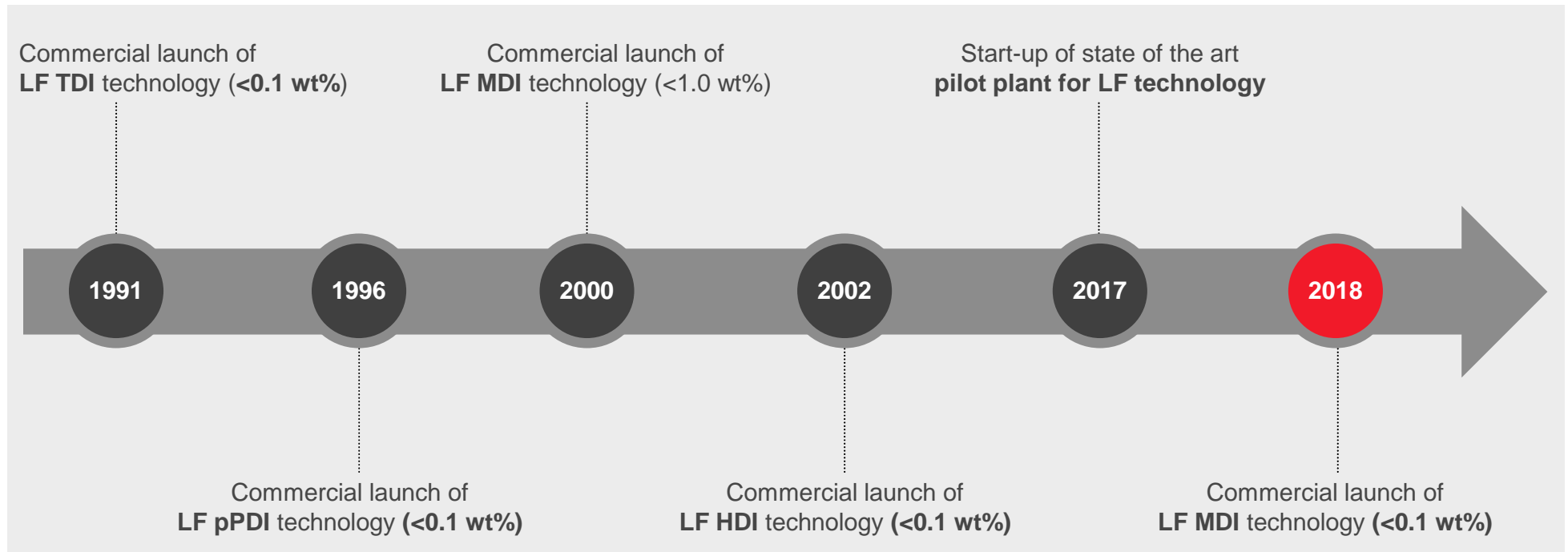


# LF technology further drives the highly structured hard segment for superior adhesive performance

Low free (LF) isocyanate prepolymers achieve narrow molecular weight distribution, virtual crosslinking, and more defined phase segregation for improved performance



# LANXESS' low free monomer technology (LF) has been developed over past decades



**As a global leader LANXESS offers the broadest portfolio of low free monomer prepolymers**

# Breakthrough innovation with <0.1% free MDI monomer prepolymers to meet regulatory requirements



## Regulatory compliant

- Protects users from potential exposure to free isocyanates
- Minimizes EH&S workload, and eliminates the handling of raw materials containing elevated levels of hazardous isocyanates
- Enables “**label-free**” formulations (reduced hazard classifications)

## Customized solution

- **Tailored viscosity and NCO content** for end-use application
- **Lower viscosity** enables use of less or no solvent in formulations
- Provides **more consistent** systems and thus consistent quality

## Excellent Performance

- Tailored chemical structure to provide **improved performance**
- **Excellent toughness**, dynamic properties, and durability
- Used in the **most demanding applications**, including adhesives, OCF, coatings, oil and gas, wheels and tires, and many others

- LANXESS is a leading innovator of Low Free (LF) isocyanate technology
- LANXESS offers leading edge LF urethane prepolymers with:
  - Levels of free isocyanate below 0.1% to address regulatory concerns
  - Wide range of chemistries

 **Adiprene® LF**  
Low Free Prepolymers

# Choice of ingredients influences performance of the final adhesives

## Enhancing functional groups expands capabilities

**Broad toolbox** allows us to vary chemistry in order to custom-design prepolymers for adhesives performance

- Isocyanate structure
- Choice of polyol and rate of crystallization
  - The molecular weight of the polyol(s)
  - The chemistry of the polyol(s) (i.e. ester or ether)
  - The linearity and functionality of the polyol(s)
- Linear vs. branched structures
- Catalyst loading
- Residual isocyanate content

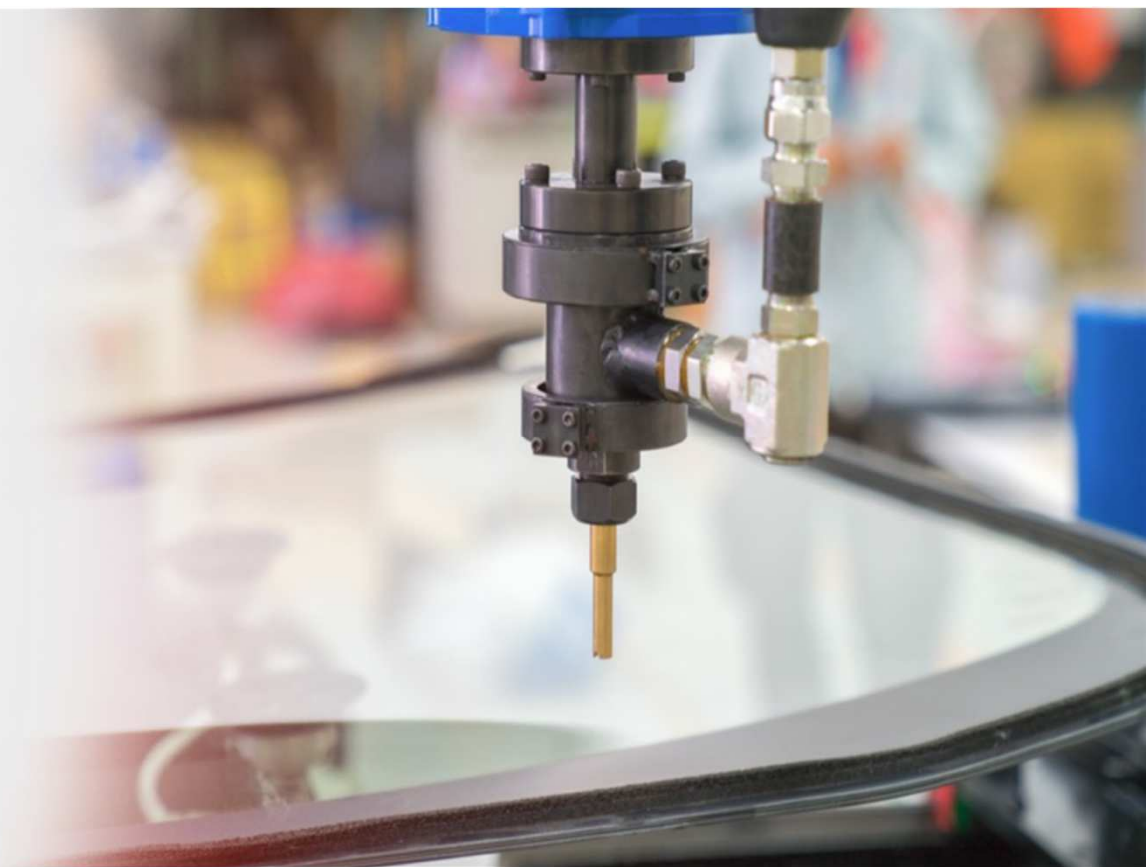
## Broad toolbox for Adhesives and Sealants

<b>Polyols</b>	<ul style="list-style-type: none"> <li>▪ Polyester: Aromatic polyesters, aliphatic polyesters, polybutadiene polyols</li> <li>▪ Polyethers: EO, PO, THF polyols</li> <li>▪ Polycarbonate polyols</li> <li>▪ Polycaprolactone polyols</li> <li>▪ Acrylic polyols</li> <li>▪ Bio-based polyols</li> </ul>
<b>Isocyanates</b>	TDI, MDI, pPDI, HDI, IPDI, H <sub>12</sub> MDI, polyisocyanates
<b>Curatives</b>	Diamines, Diols, Triols
<b>Additives</b>	Catalysts, antioxidants, plasticizers, flame retardants, pigments, and fillers

**LANXESS Urethane Systems supports innovation with customized urethane systems for adhesives**

# Agenda

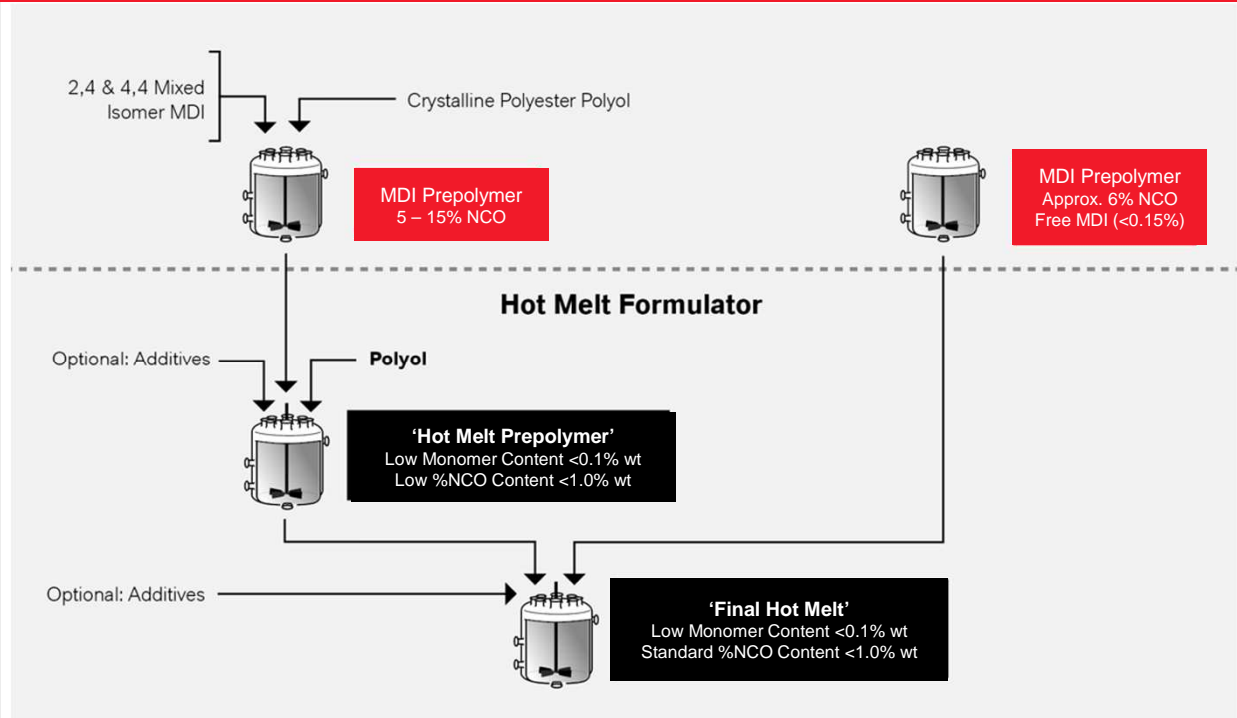
1. About LANXESS Urethane Systems
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# Established way for low monomer hot melts (<0.1%) involves a lengthy process using two prepolymers

## Established approach for low monomer hot melt products

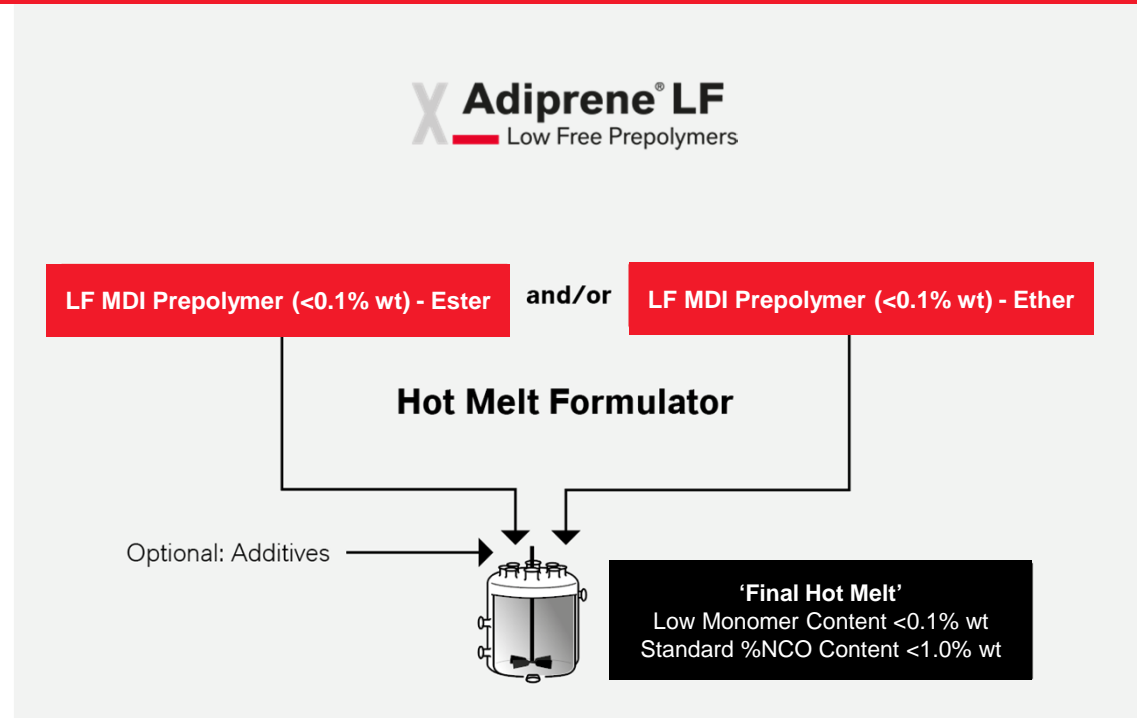
- Multi-step process involving two prepolymers
- Limited flexibility by using a conventional prepolymer
- Tailoring viscosity more difficult (processability)
- High levels of industrial hygiene management required during formulation
- Intensive analytic quality control to ensure <0.1% free isocyanate content in formulation



# LANXESS offers full low monomer approach for flexible and customized “label-free” hot melts

## LANXESS Adiprene® low monomer approach to hot melts

- Elimination of complexity (short process)
- Fully flexible hot melt formulation using Adiprene® LF MDI prepolymers only
- High degree of customized prepolymer formulations possible
- Blending of two Adiprene® LF MDI prepolymers with flexible mixing ratios gives access to a range of different hot melt formulations
- Improved industrial hygiene by avoiding handling of free monomeric isocyanate during formulation and final hot melt use
- Enables formulation of “label-free” products

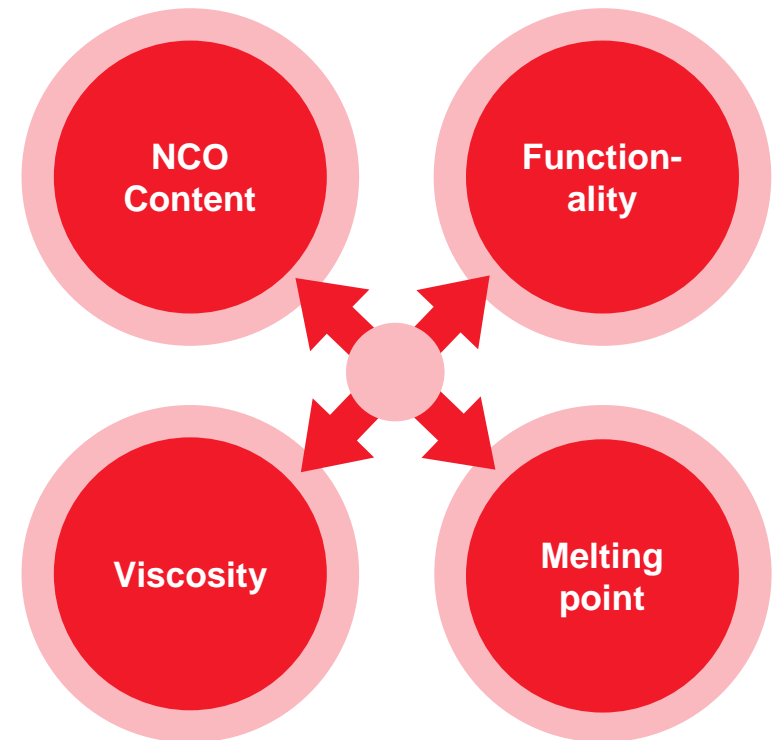




# Challenges for Adhesives & Sealants formulators arising from using low monomer formulations

## Take away from Adhesives formulators

- Free monomer in conventional systems contributes significantly to the NCO content of the prepolymer product
- Removal of free monomer makes it difficult to achieve high NCO prepolymers
- Free monomer also contributes to reactivity and viscosity at application temperature



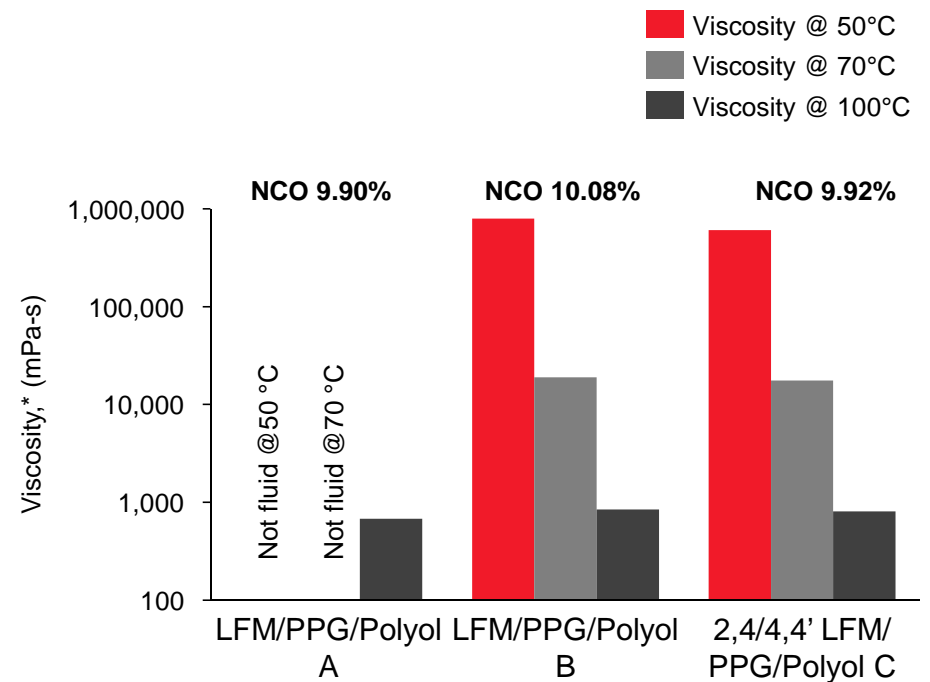
# Exploration of high NCO LF MDI prepolymers shows importance to control morphology

## Successful synthesis of low monomer MDI prepolymer with up to 10% NCO

- NCO content of low monomer prepolymers is governed by structure and polyol molecular weight
- Low MW polyols incorporated into prepolymers can become very crystalline, resulting in high melting/high viscosity systems
- Challenge is to formulate to overcome/compensate for this high crystallinity

### ENHANCED PERFORMANCE

High NCO content can lead to adhesives with **improved physical and mechanical properties** for demanding applications



# Ability to tailor LF prepolymer to the needs of the application, especially important for reactive hot melts

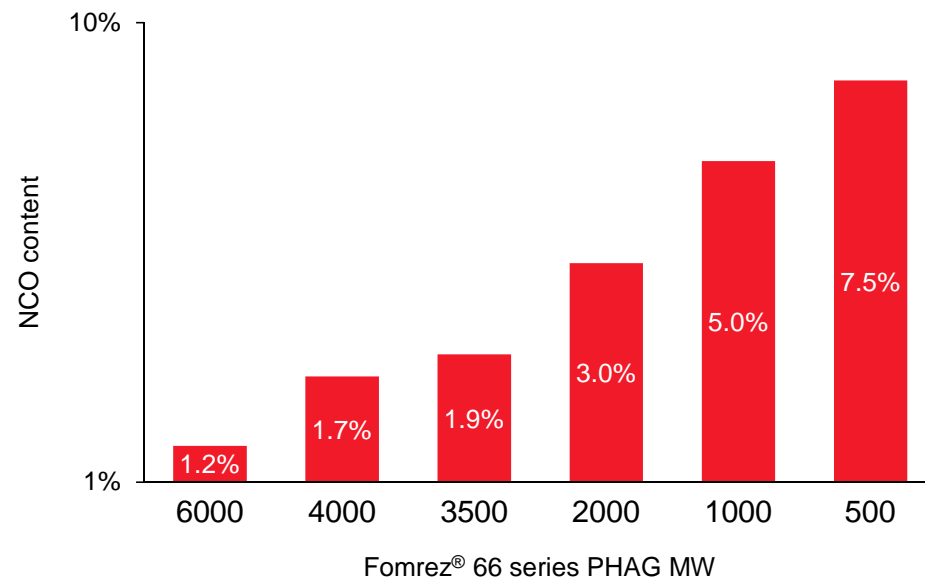
## Range of LF MDI prepolymers based on Fomrez® 66 series

- Fomrez® 66 series are polyester polyols
  - Poly(hexamethylene adipate) glycol (PHAG)
  - Highly crystalline
- Diverse range of Fomrez® 66 polyols enables formulation of Low Free MDI prepolymers with NCO contents ranging from 1.2% to 7.5%

### LOW VISCOSITY

LF technology and associated formulation knowledge enables lower viscosity at working temperature

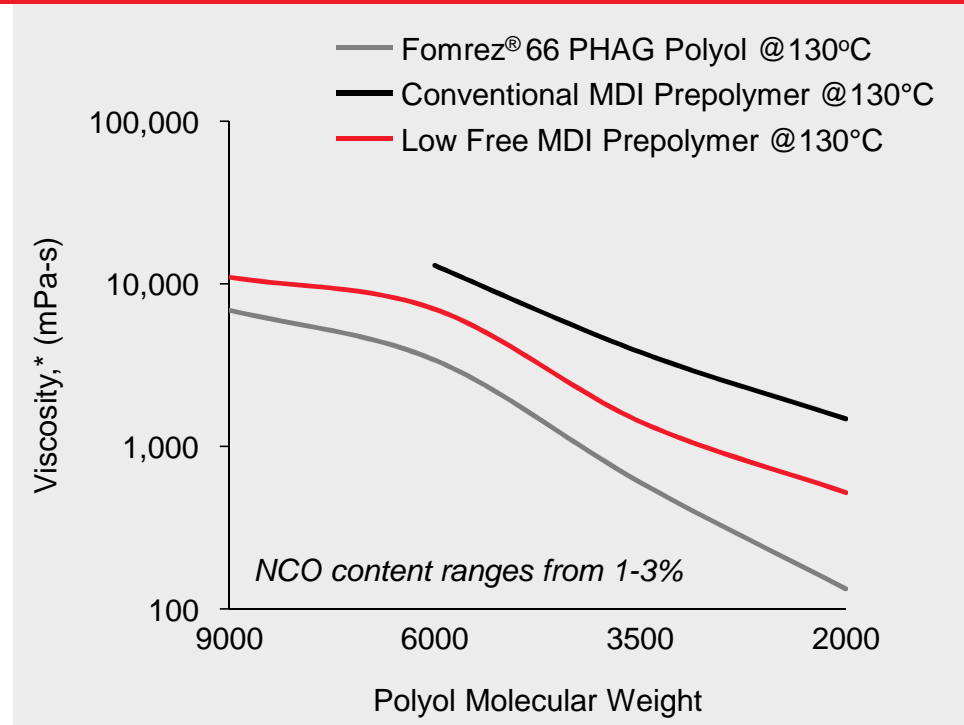
Fomrez® 66 series Polyester Polyols based on PHAG



# Low Free isocyanate urethanes improves use of highly crystalline polyols, up to 9000 molecular weight

## Ability to incorporate extremely high MW, highly crystalline PHAG polyols into the backbone

- Initial bond strength develops faster with higher MW polyols, which will crystallize faster upon cooling
- Reduced viscosity even with solid, crystalline polyols for applications like reactive hot melts
  - Can work at lower temperatures
  - Improved wetting, better flow, less joining force needed
- Simplifies formulation of low viscosity reactive hot melt adhesives with <0.1% free MDI
  - Reduces or eliminates need for diluting additives to achieve low monomer or lower viscosity levels
  - Use any MDI type: 2,4' or 4,4' or combination
  - Wide range of NCO content can be achieved

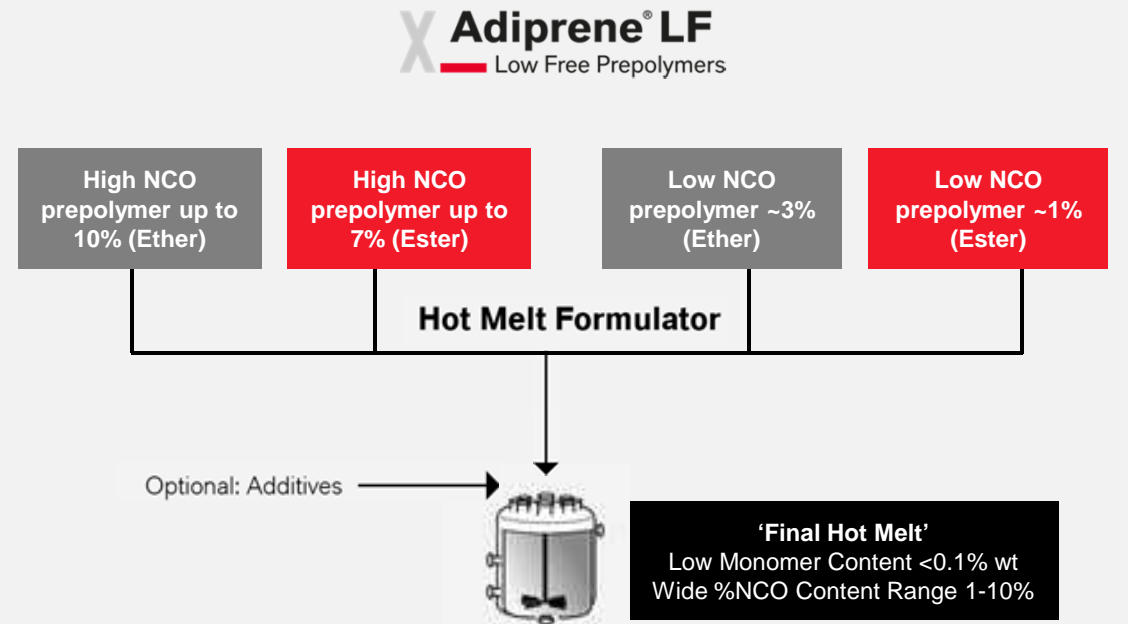


Note: 9000 MW was not tested as a conventional prepolymer due to extremely high viscosity  
\* Data is specific to specimens tested

# LANXESS offers full formulation platform for low monomer, “label-free” hot melt adhesives

## LANXESS Adiprene® low monomer platform for hot melts

- LF prepolymer technology offers flexible formulation platform
- Wide range of NCO content possible 1-10% with ether and ester based prepolymers
- Either 4,4' MDI or 2,4 & 4,4' mixed MDI prepolymers for tailored reactivity
- All prepolymers with <0.1wt% of free diisocyanate monomer – **storage stable!**
- Use of LF prepolymers reduces the dependency of using 2,4 MDI prepolymers for viscosity reduction



# Exploration of increased functionality prepolymers indicates potential but needs further development

## Conclusion on first results

- Prepolymers with increased functionality incorporate cross-linking into the polyurethane backbone
- Cross-linking can increase strength/rigidity in adhesive formulations
- Incorporating higher functionality into the prepolymer backbone can result in highly cross-linked systems that have very high melting points
- Challenge is to formulate increased functionality into the prepolymer backbone without yielding high melting point

LF MDI  
Tri-functional  
PPG

- Successful synthesis and free monomer removal
- Resulting prepolymer has a melting point above 80 °C

LF MDI  
Tetra-functional  
PPG

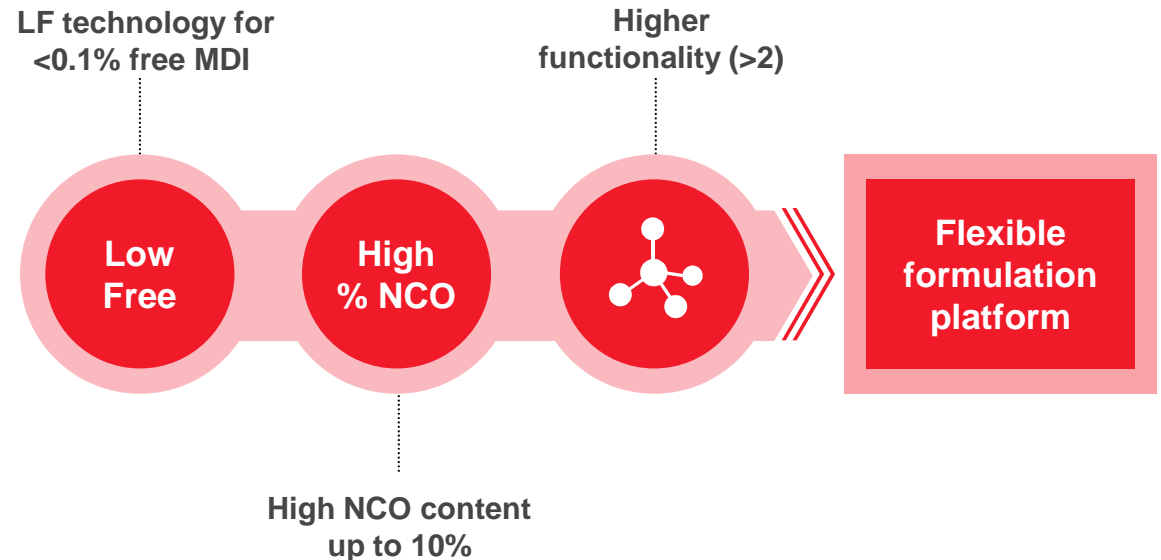
- Successful synthesis and free monomer removal
- Resulting prepolymer melting point above 80 °C

LF MDI  
PPG/  
Tri-functional  
PPG

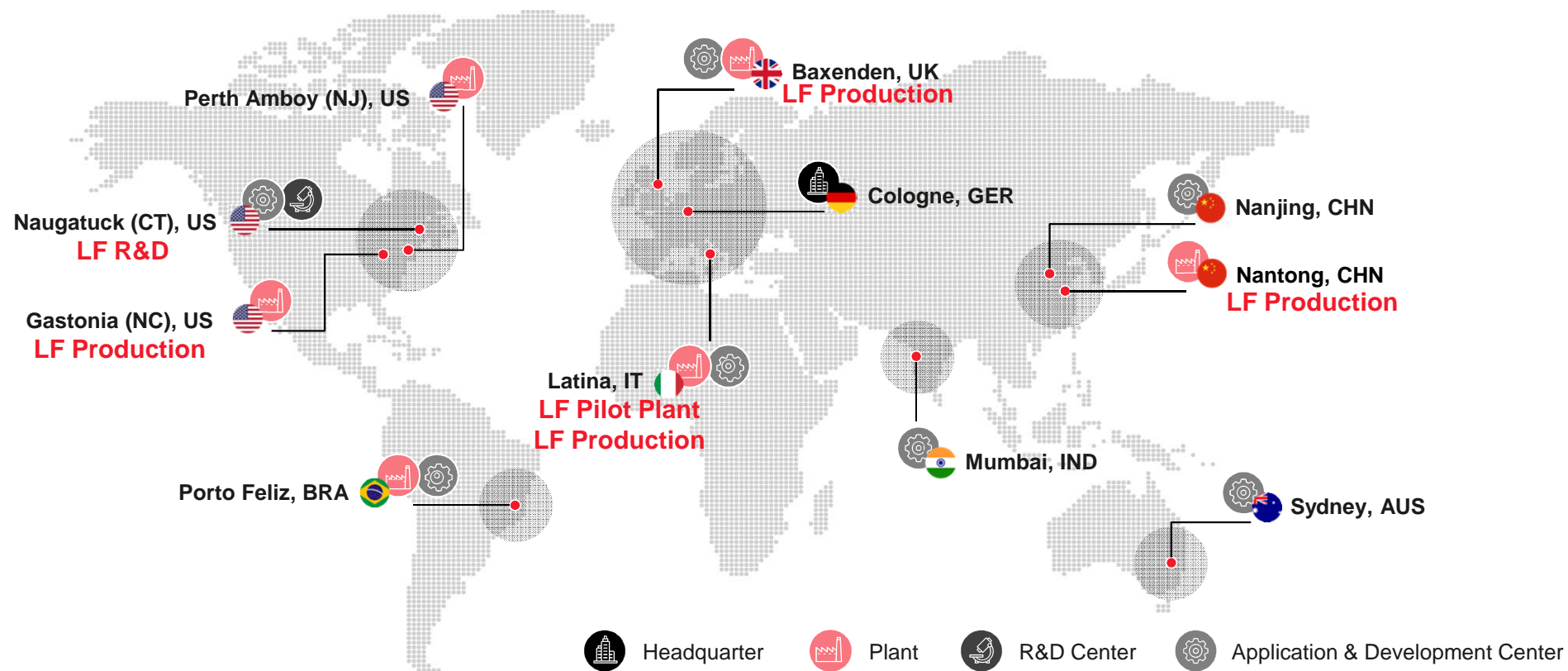
- Successful synthesis and free monomer removal
- Resulting prepolymer melting point above 80 °C

# Lanxess drives development of powerful low monomer prepolymers used as flexible building block

- **Low Free prepolymer technology** offers **flexible formulation platform**
- **Higher functionality** prepolymers lead to higher crosslinking and increase strength/rigidity in adhesive formulations
- **High NCO** content can lead to adhesives with improved physical and mechanical properties for demanding applications
- LF technology and associated formulation knowledge **enables lower viscosity** at working temperature
- All prepolymers with <0.1wt% of free diisocyanate monomer – **storage stable!**



# LANXESS has global LF prepolymer capabilities across R&D laboratory, pilot plant, and full scale production





**QUALITY WORKS.**

**LANXESS**

Energizing Chemistry

# Disclaimer



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Unless specified to the contrary, the values given have been established on standardized test specimens at room temperature. The figures should be regarded as guide values only and not as binding minimum values. Kindly note that the results refer exclusively to the specimens tested. Under certain conditions, the test results established can be affected to a considerable extent by the processing conditions and manufacturing process.

