Dow Industrial Solutions

A New Preformed Polyurea Thickener for Grease

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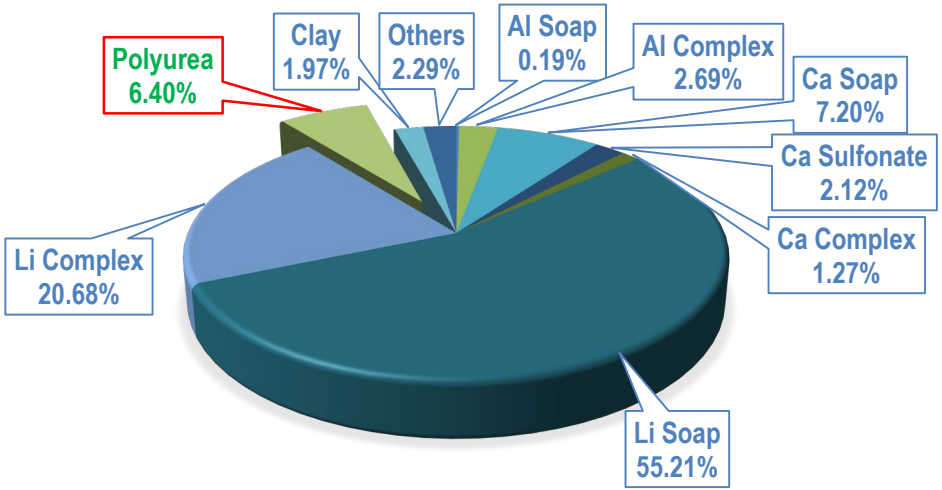
Grease Market Overview

- Grease = **Thickener** + Base Stock + Additives
- Total grease production was about 2.57 BM lbs in 2016 (1.4% increase from 2015)
  - Polyurea thickened greases account for approximately 158 MM lbs with a market share of 6%

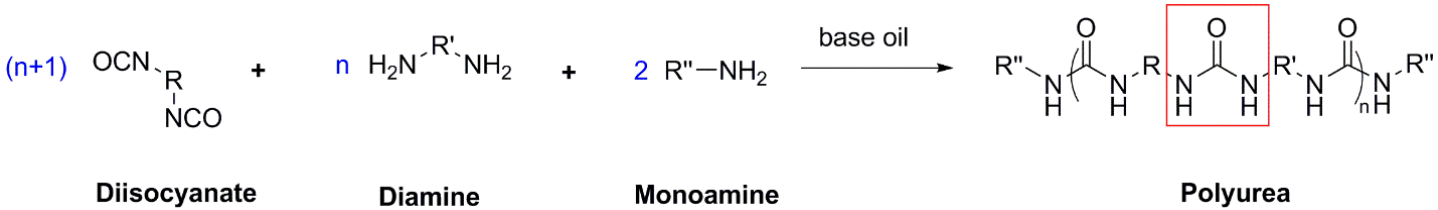


2016 NLGI Grease Production Survey - Total Grease Survey

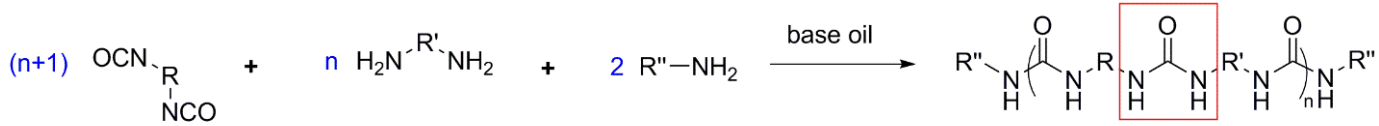
Polyurea Greases

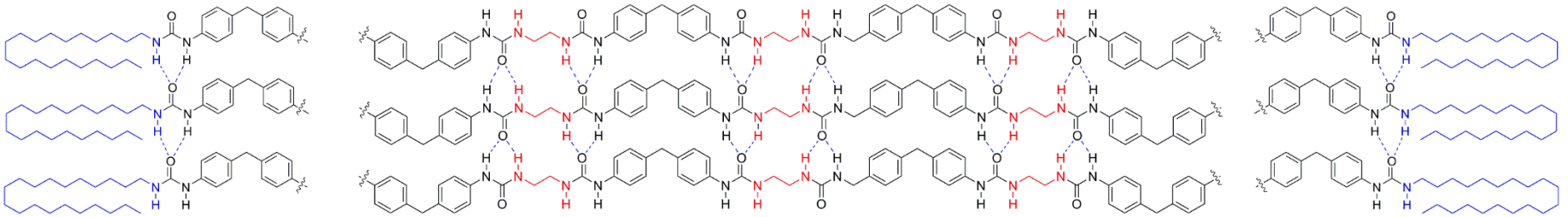
- **<u>Primary Applications</u> for Polyurea Greases: high temperature, anti-oxidative and fill-for-life applications (e.g. CVJ, electric motor bearings, etc.)**
  - Market demands high performance grease
  - Less availability and increasing price of LiOH
  - Limited by the toxicity of the raw materials and handling complexity

- **Predominant *in situ* technology (isocyanate + amine reacted *in situ* in the base stock)**



Polyurea Chemistry Overview





- Reaction takes place in the base stock
- Isocyanate + (diamine linkage) + alkyl / alicyclic / aromatic amine tail → often are diureas and tetraureas
- **Thickener microstructure** is very important (H-bonding, dispersibility and mechanical stability, etc.)

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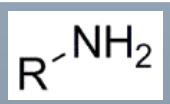
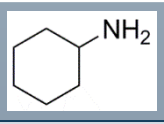
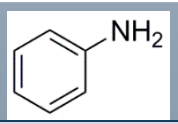
Structure vs. Property

Chemical structure of thickener has a significant impact on grease properties

Structure Selection v.s. Grease Properties			
Amine end group			
Thickening efficiency	-	+	++
Thermal stability	-	+	++
Shear stability	-	+	++
Pumpability	++	+	-

- TDI and MDI are most commonly used isocyanates
- More variations provided by choice of amines
- Usually a combination of amine/isocyanates used in formulation to achieve structure complexity

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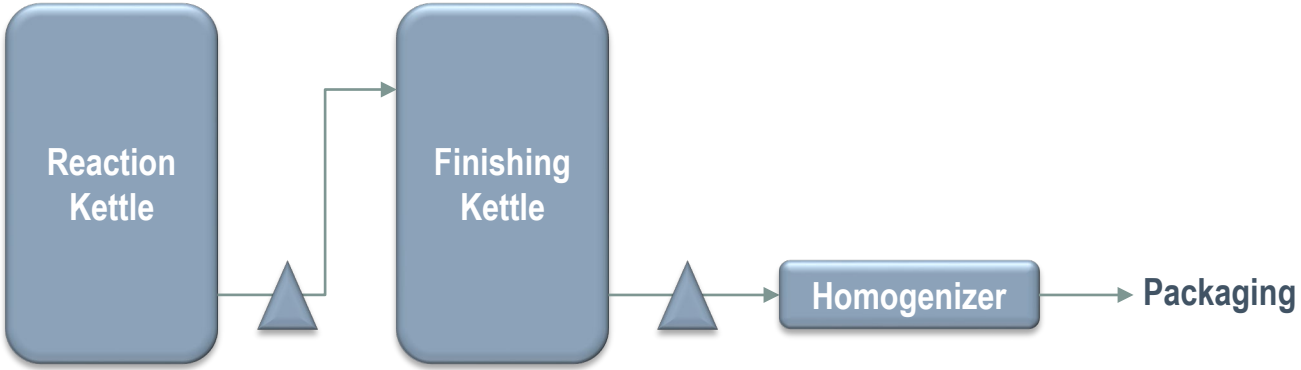
In situ Manufacturing Process



- Mixing and dispersion process is important to achieve desired consistency and completion of reaction
- Manufacturing can be difficult due to health hazards of raw materials
- Specially designed facilities are required to effectively handle the reaction of toxic raw materials

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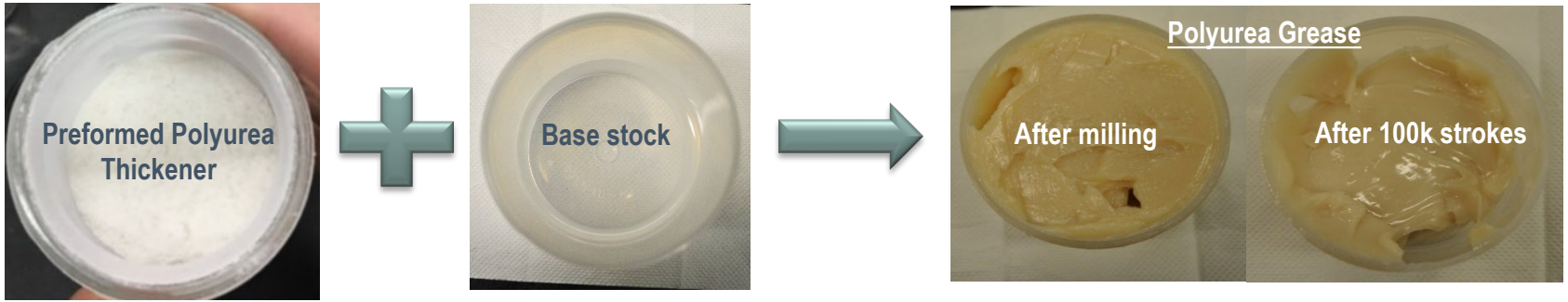
Preformed Thickener Technology



- Less hazardous raw material handling for grease manufacturers
- May not require special equipment to handle toxic raw materials
- Standard Li grease kettle may be used to formulate polyurea grease
- Reduce batch to batch variation from *in situ* production
- Tailor the thickener structure according to specific needs

This **preformed polyurea thickener** will provide an alternative for polyurea grease production with competitive lubricating properties, and enhanced safety & handling benefits

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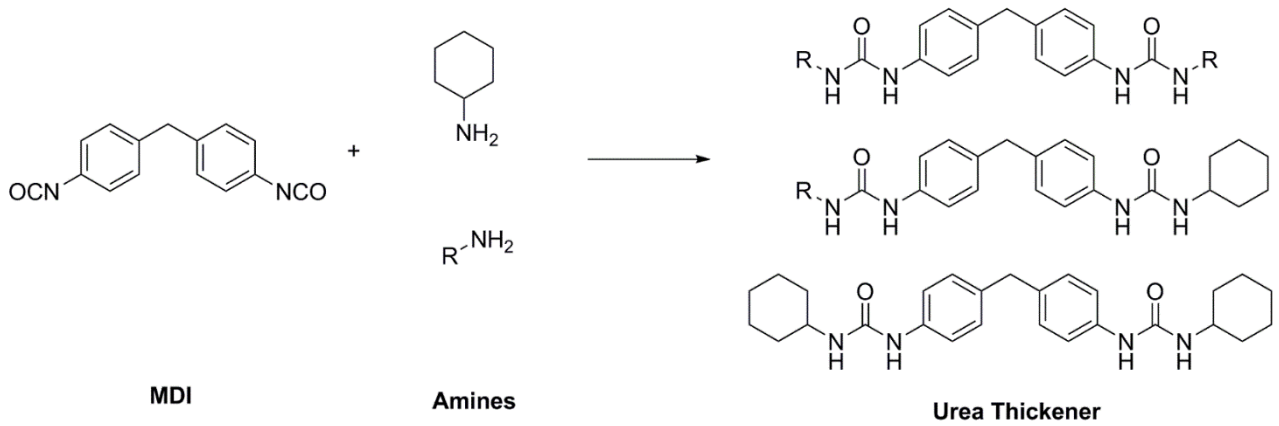
Preformed Thickener Structure

Model compound used for this study

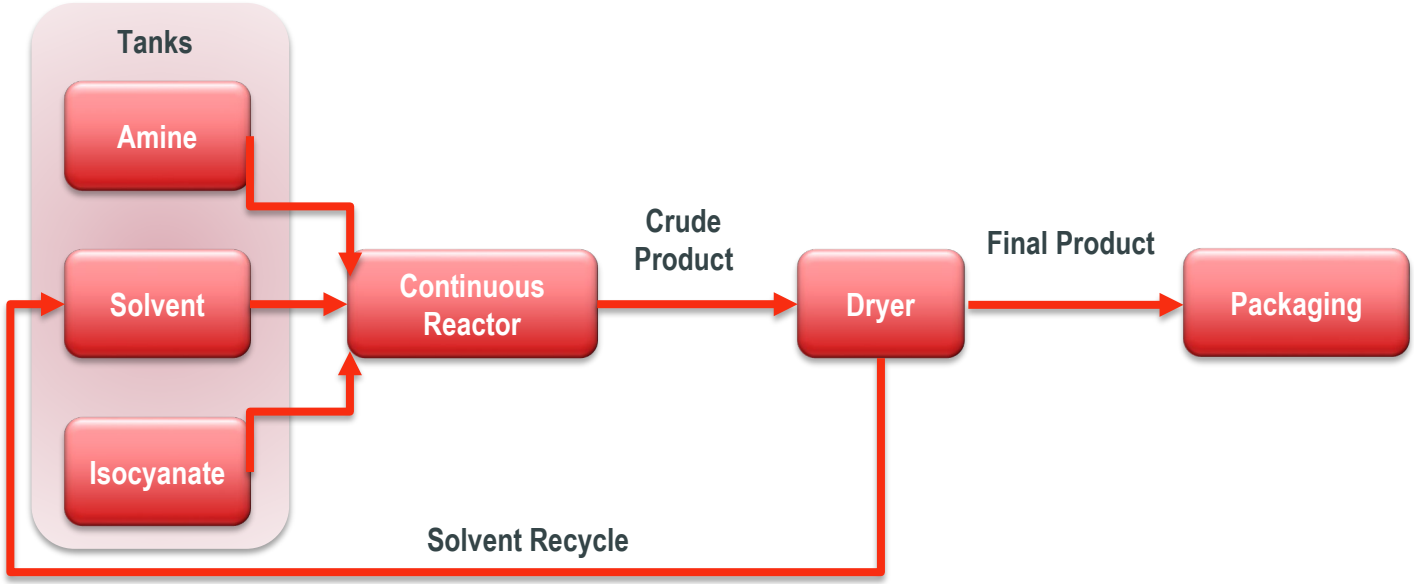


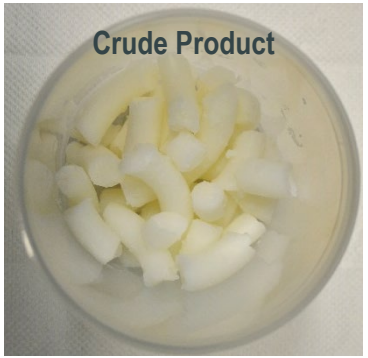
R = aliphatic alkyl group
Other urea structures were also made

Straightforward chemistry but difficult to operate:

- Hazardous raw materials
- Exothermic – urea bond formation generates ~ 40 kcal/mol
- Fast kinetics – hard to achieve stoichiometric reaction

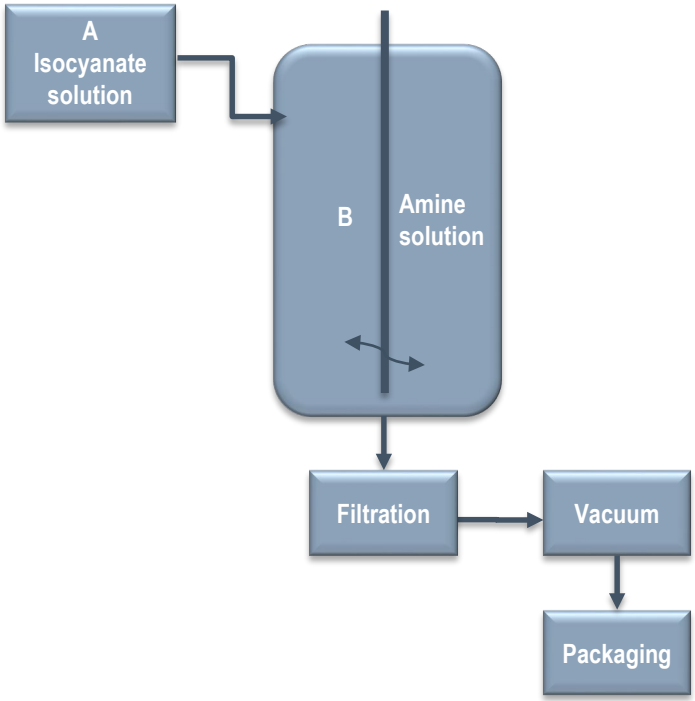
Dow Process Technology*

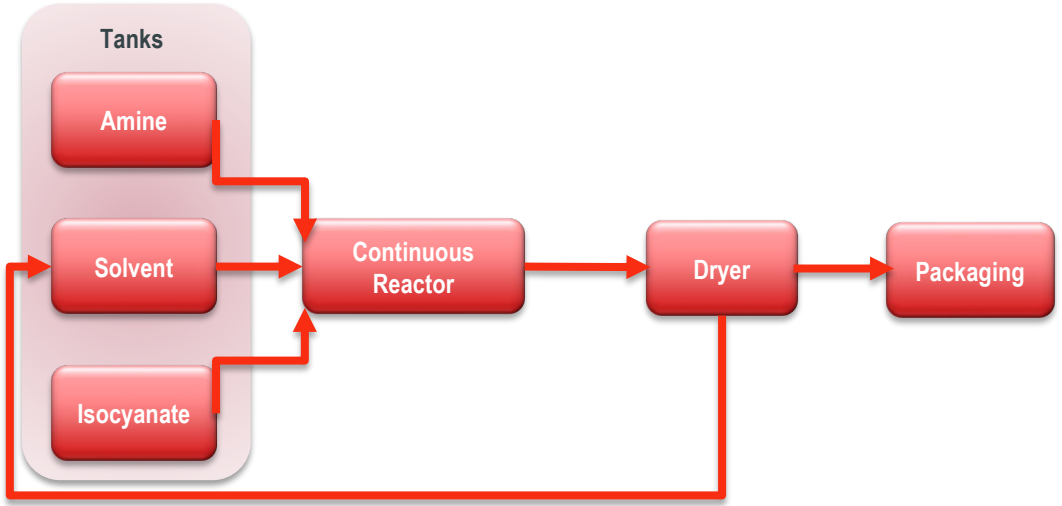




*Patent pending

Batch Process v.s. Continuous Process





- ✓ Flexible process to give various thickener structures
- ✓ Highly reliable process
- ✓ Controllable reaction
- ✓ Uniform particle size

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Preformed Polyurea Thickener Overview

Specs	Target	Performance
Unreacted raw materials	<0.1 wt% free isocyanate; <1 wt% free amine	Pass
Residual Solvent	<0.5 wt%	Pass
Particle size distribution	Narrow distribution, agglomerates <500 µm	Pass
Shear stability	NLGI grade 2 with 12.5% thickener loading; Penetration increase <15% after 100k strokes	Exceed - NLGI grade 3 with 12.5% thickener loading; <9% penetration loss after 100k strokes
Dropping point	240 ºC	> 260 ºC (exceed instrument detection capability)

- ✓ Dow proprietary process technology
- ✓ Enhanced thickening efficiency and shear stability v.s. batch process
- ✓ High process flexibility → Enable tuning of thickener structure according to needs


Thickener appearance

Grease application guide
ASTM D217 - Standard Test Methods for Cone Penetration of Lubricating Grease
ASTM D2265 - Standard Test Method for Dropping Point of Lubricating Grease Over Wide Temperature Range

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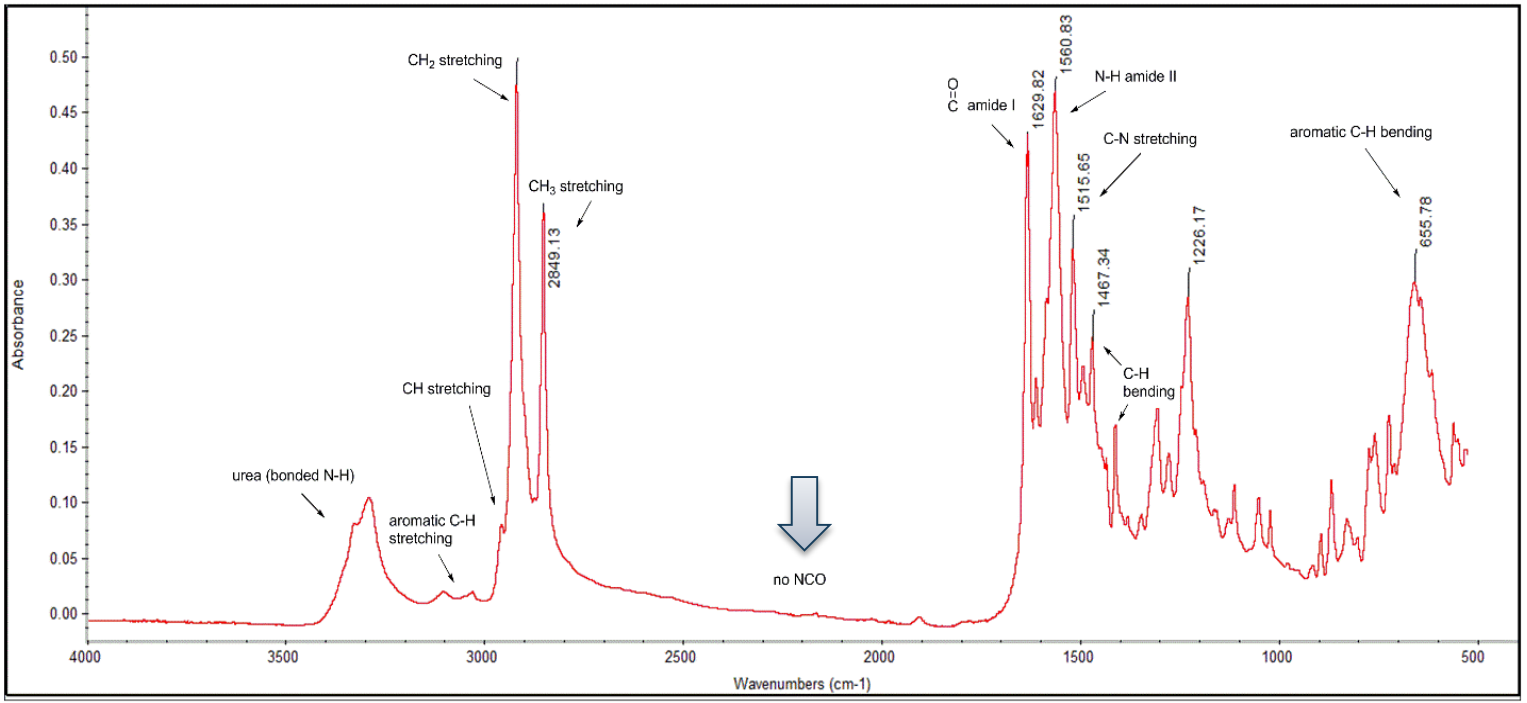
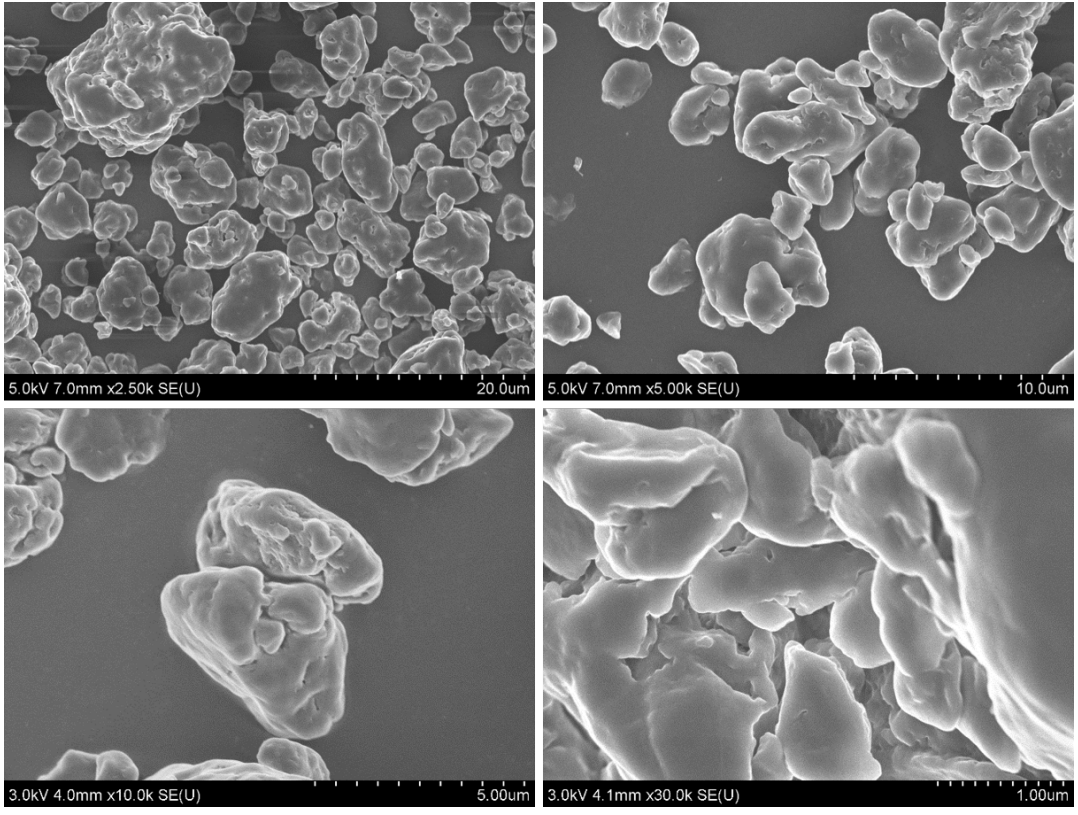
Material Characterization – FTIR

No residual isocyanate

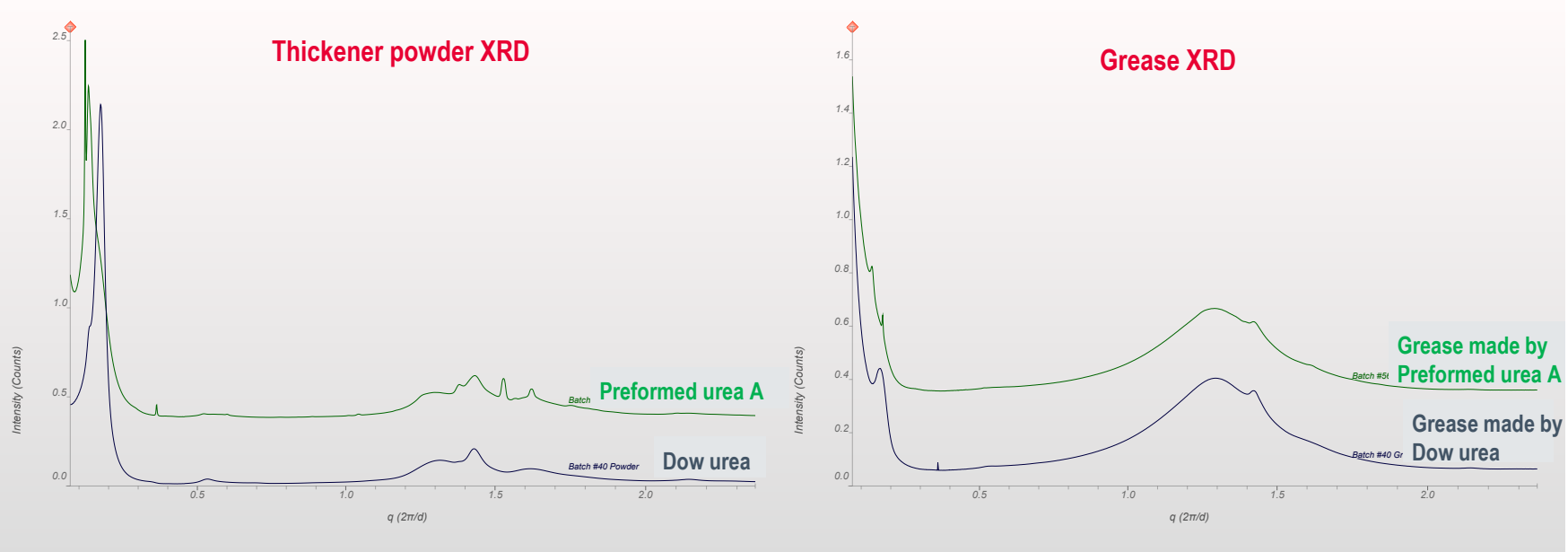


Material Characterization – SEM

Narrow particle size distribution



XRD of Preformed Thickener and Grease



- XRD shows difference in both preformed thickener powder and grease
- Slightly higher average spacing and narrower distribution for the high level structure observed in Dow urea
- Grease made by Dow urea presents slightly higher crystallinity
- Higher level structure gives different spacing in the grease made by Preformed urea A and Dow urea

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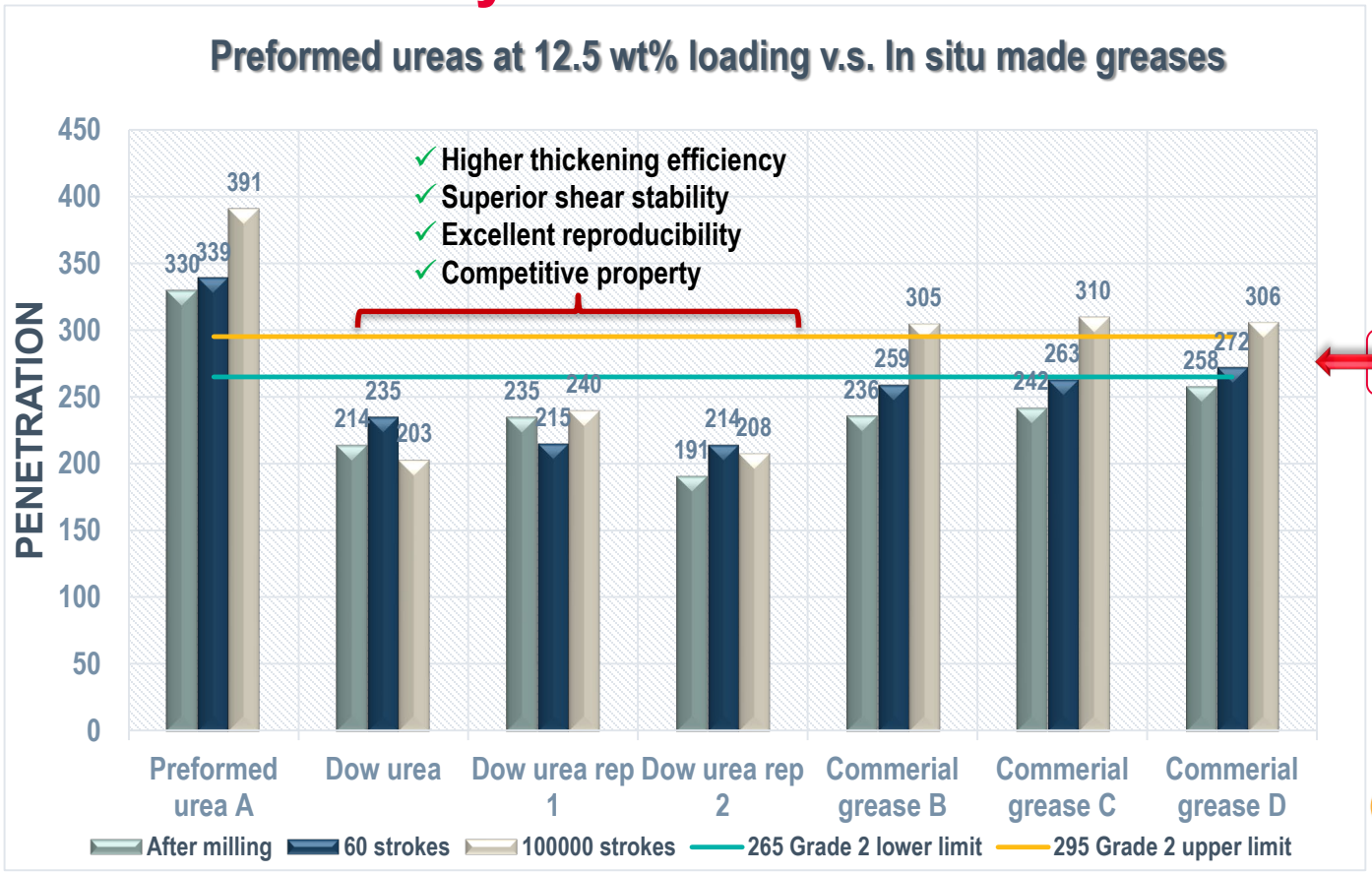
Grease Shear Stability



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Roll Stability Test

	ASTM D1831			ASTM D1831 Modified		
	ASTM D1403 Original Worked Penetration	ASTM D1403 Worked Penetration After Rolling	Δ	ASTM D1403 Original Worked Penetration	ASTM D1403 Worked Penetration After Rolling	Δ
Dow urea *	211	206	-5	211	191	-20
Preformed urea A *	315	355	40	315	374	59
Commercial grease B	268	292	24	268	332	64
Commercial grease C	266	300	34	266	328	62

** Greases made by Dow urea and Preformed urea A are unformulated with 12.5% thickener loading in Group II mineral oil. Made through the same procedure*

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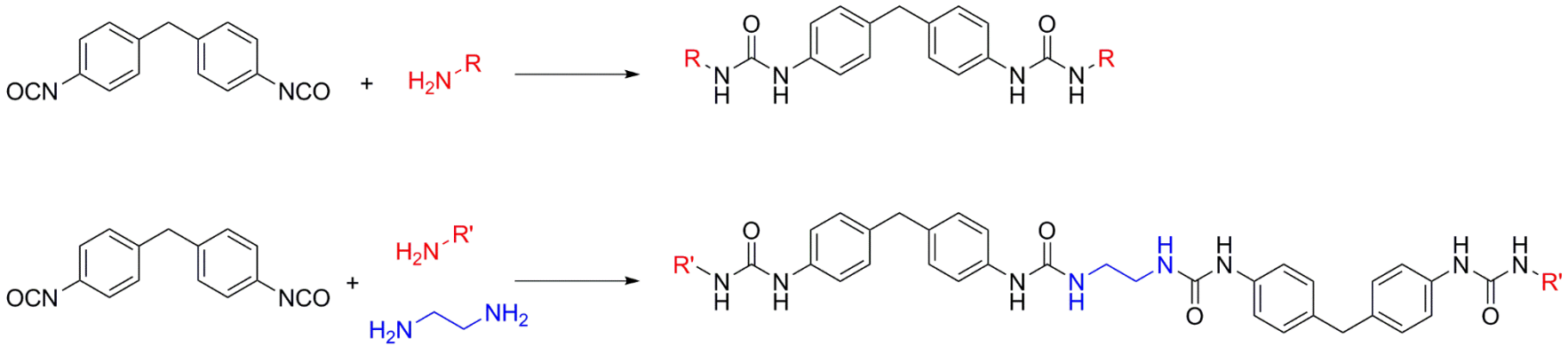
Thickener Structure Variations

Flexible process can produce customized thickener structures



R and R'= aliphatic alkyl, alicyclic, or aromatic group

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Flexible Process Enables Tailored Products

to meet registration requirements

Polyurea Thickener	Structure	Inventory
Preformed thickener 1	MDI based diurea, asymmetric	US, Canada, Australia, Taiwan
Preformed thickener 2	MDI based diurea, asymmetric	US, EU, China, South Korea, Philippines, Taiwan
Preformed thickener 3	MDI based diurea, symmetric	US, Canada, South Korea, Taiwan
Preformed thickener 4	MDI based diurea, symmetric	US, EU, China, South Korea, Philippines, Taiwan

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Conclusions

This work reports the development of a multi-component polyurea mixture designated for lubricating grease application. It is produced through a novel continuous synthesis of isocyanates and amines, and can be offered as a preformed thickener for the manufacture of polyurea grease.

This novel process presents high flexibility and enables tailored product. NLGI Grade 3 grease can be made with 12.5% thickener loading. The resulted grease also shows enhanced thickening efficiency and shear stability

This preformed polyurea thickener will provide global lubricating grease market an alternative for polyurea grease production with competitive lubricating properties, and enhanced safety & handling benefits

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Thank you!

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