

**COATINGS AND FILMS WITH EXPANDED USABILITY MADE  
FROM NOVEL SOLVENT-FREE POLYURETHANE DISPERSIONS**

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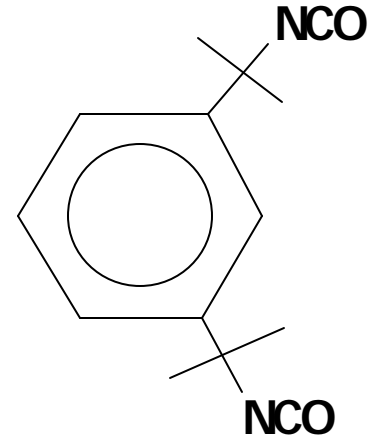
# Outline

- ? Introduction
  - Polyurethane dispersion (PUD) process stages, choice of diisocyanate
  - New polyols for PUD manufacturing
- ? Heat-sealable coatings
  - Effect of polyester polyol melting on activation temperature and blocking resistance
  - Polymer rheology and adhesive performance
- ? Exceptionally hard coatings.
  - Effect of polyol melting and glass transition temperatures on surface hardness
- ? Elastic films/Soft coatings
  - Low modulus, high elongation films
- ? Conclusions

# PUD - choice of isocyanate

TMXDI advantages

TMXDI<sup>®</sup> (META) –  
meta-tetramethylxylylene diisocyanate



- ? PUD production without use of any solvent using simple prepolymer mixing process
- ? near “zero-VOC” product
- ? better through-put (reactor utilization)
- ? use of higher molecular weight polyester,
- ? use of high-melting polyols

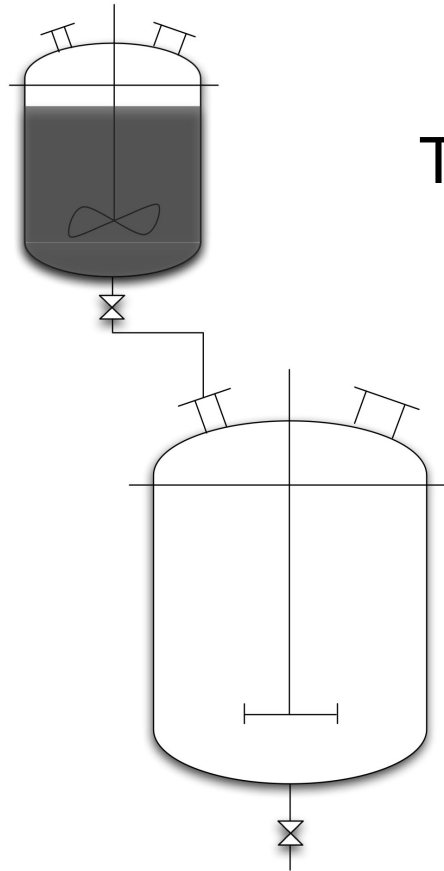
Environmentally Friendly Solutions

# PUD process:

prepolymer preparation temperature

aromatic diisocyanates –  
50-60°C

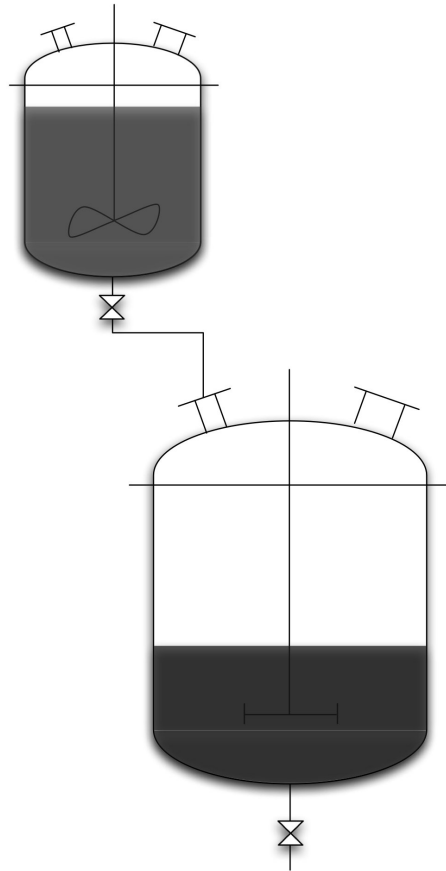
aliphatic diisocyanates –  
80-100°C



TMXDI – up to 150°C

# PUD process:

temperature of water



aromatic diisocyanates –

5-10°C

aliphatic diisocyanates –

20-30°C

TMXDI – up to 90°C!

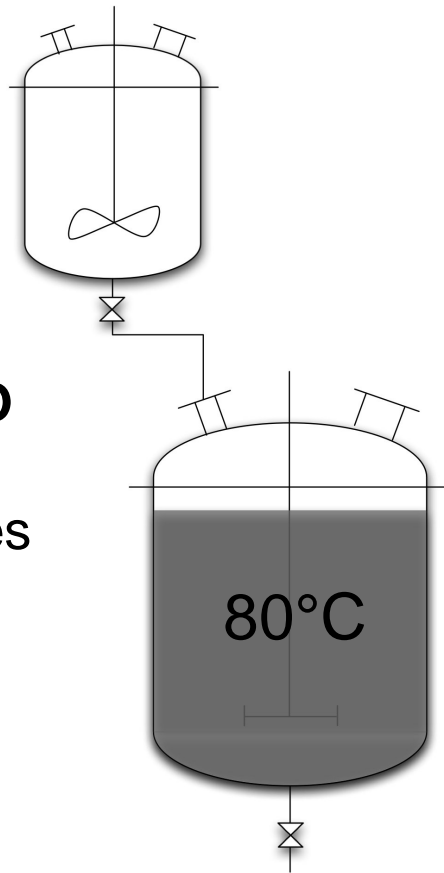
# PUD process:

dispersion temperature

with TMXDI, there is:

? **minimal loss of NCO**  
during dispersion  
process at temperatures  
as high as 80°C!

? minimal CO<sub>2</sub> release  
due to slow reaction of  
NCO with water ?  
**negligible foaming**



TMXDI-based  
prepolymer with free  
NCO functionality is  
stable in water at  
room temperature for  
days, even weeks!

# New polyols for PUD

- ? **co-polyesters of tere-phthalic acid** – heat-sealable coatings, e.g. credit card adhesive with excellent blocking resistance, high heat resistance, improved adhesion to certain substrates
- ? high-viscosity polyols, like **co-polyesters of adipic and phthalic acids** – elastomeric films and coatings with outstanding strength.
- ? **polyols with high melting and glass transition temperatures** – coatings with outstanding surface hardness
- ? combination of **crystalline and amorphous polyesters (high melting)** – coatings with unique soft or “silky” feel.
- ? **modified polyolefin waxes** (maleated, carboxylated) as building blocks for aqueous polyurethanes could improve chemical resistance and adhesion to non-treated polyolefins.

New polyols = new opportunities

# Prepolymer viscosity comparison

(NCO/OH = 1.6, DMPA = 4.5%).

| Polyester | Isocyanate          | Viscosity @ 90°C,<br>cPs | Viscosity @ 120°C,<br>cPs |
|-----------|---------------------|--------------------------|---------------------------|
| HA 2000   | TMXDI               | <b>8260</b>              | no data                   |
|           | IPDI                | 16400                    | no data                   |
|           | H <sub>12</sub> MDI | 40000                    | no data                   |
| BA 2000   | TMXDI               | <b>7710</b>              | no data                   |
|           | IPDI                | 19500                    | no data                   |
|           | H <sub>12</sub> MDI | 34300                    | no data                   |
| HAT 3500  | TMXDI               | solid                    | <b>35000</b>              |
|           | IPDI                | solid                    | *                         |
|           | H <sub>12</sub> MDI | solid                    | *                         |

\* - prepolymer could not be prepared

Brookfield Viscometer DV-II with Thermosel unit, spindle 27 @ 5 rpm

HA - hexanediol adipate; BA - butanediol adipate; HAT - hexanediol adipate/terephthalate

# Heat-sealable coatings

## outline

- ? Effect of polyester polyol melting on activation temperature and blocking resistance
  - molecular weight of polyester
  - melting temperature
- ? Polymer rheology and adhesive performance
  - $E'$ ,  $\tan \delta$  as measure of blocking and heat resistance

# PUD for heat sealable coatings

performance characteristics

Applications: film lamination, shoe bonding

TMXDI allows for:

? higher molecular weight polyester

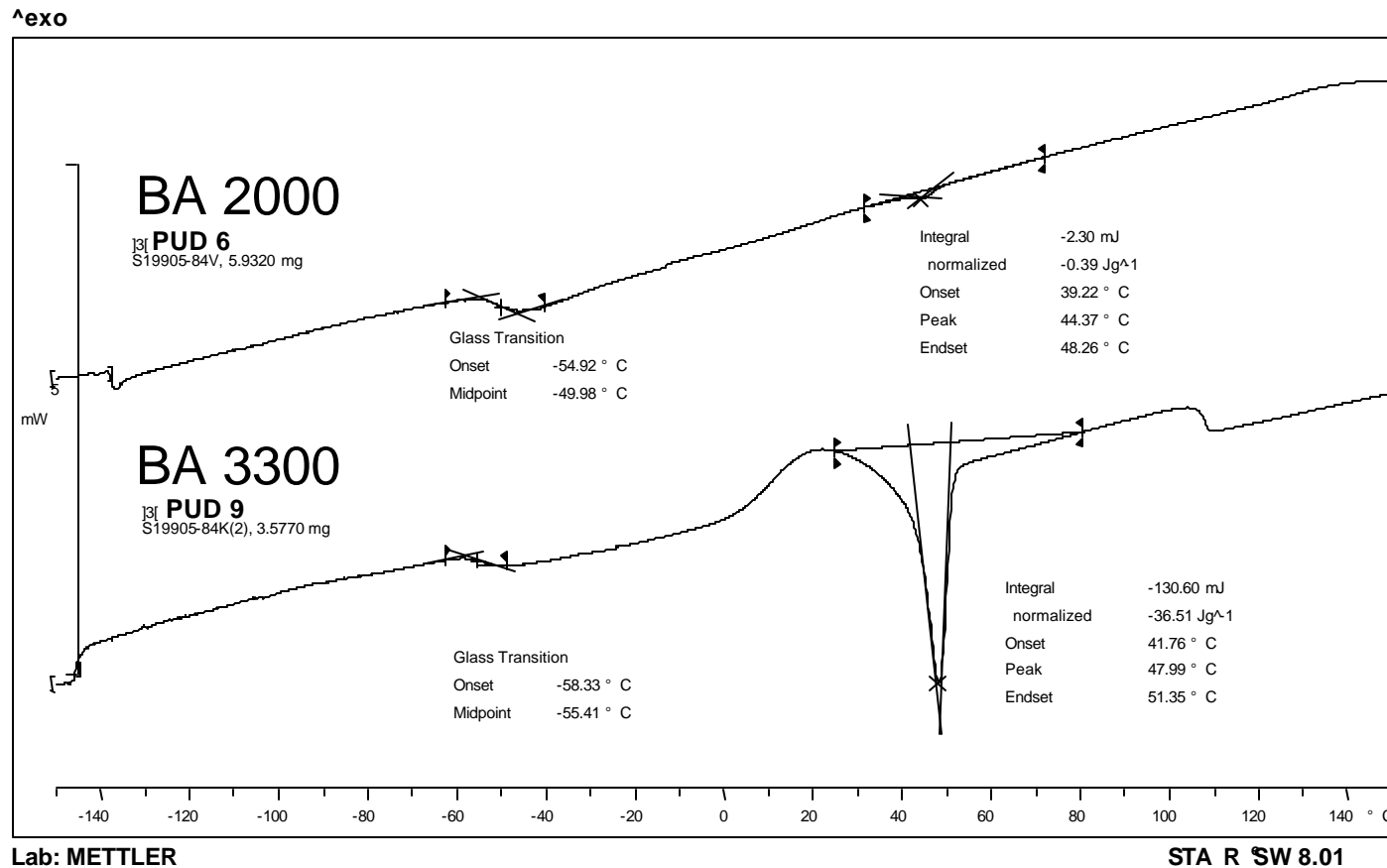
- sharper activation
- improved blocking resistance

? higher melting temperature polyester

- higher activation temperature
- further improved blocking resistance
- excellent heat resistance

# Molecular weight effect ...

DSC curve for PUD film made with BA 2000 & BA 3300



# Heat-seal adhesive

polymer rheology - performance characteristics

Cohesive strength and surface hardness of the adhesive coating can` be related to a certain value of storage modulus and  $\tan \delta$ .

- ? Acceptable blocking resistance –  $E' > 10 \text{ MPa}$  (estimate from available data).
  - The temperature, at which storage modulus reaches 10 MPa level, can be used for estimation of blocking resistance of the heat-sealable coating.
  - Higher molecular weight polyol - advantageous combination of storage modulus and  $\tan \delta$  at higher temperature, which translates in improved blocking resistance.

# Heat-seal adhesive

## polymer rheology - performance characteristics

With TMXDI - PUD can be successfully prepared at temperatures high enough to utilize terephthalic acid-based polyols, such as hexanediol terephthalate, which melts at about 105°C.

- ? Activation temperature from Dahlquist Criterion (shear storage modulus  $G' < 5 \times 10^5$  Pa or tensile modulus  $E' < 1$  MPa)
  - at 54-58°C for adipates (PUD 9)
  - 60-67°C for terephthalates (PUD 15).
- ? Heat activation shifts to higher temperature, which is still in commonly used range
- ? Higher melting point - excellent blocking resistance and higher heat resistance properties
- ? DMA allows to estimate real-life performance.

# Heat-sealable coating

peel adhesion and blocking resistance test data.

| PUD | polyol   | 180° peel adhesion |      |       |       | blocking 1 | blocking 2 |
|-----|----------|--------------------|------|-------|-------|------------|------------|
|     |          | 60°C               | 80°C | 100°C | 120°C |            |            |
| 6   | BA 2000  | 2.4                | 6.6  | 10.9  | -     | 1          | 0          |
| 9   | BA 3300  | 0.6                | 4.6  | 18.9  | -     | 3          | 0          |
| 15  | HAT 3500 | -                  | 0    | 14.9  | 23.8  | -          | 5          |

BA - butanediol adipate; HAT - hexanediol adipate/terephthalate

blocking 1 - overnight @ 45°C/50 lbs.

blocking 2 - three days @ 50°C/50 lbs.

blocking rating: 0 = worst (substrate tear), 5 = best (separates easily)

# DMA data - E', tan d

for PUD's made with BA of different molecular weight

Blocking and heat resistance is better when storage modulus (hardness) is higher and loss modulus is lower (cohesive strength).

In other words, better heat and blocking resistance should be expected for polymers showing higher storage modulus and lower tan d at the temperature of interest.

| PUD | Polyol mol. wt. | 40°C |       | 50°C |       |
|-----|-----------------|------|-------|------|-------|
|     |                 | E'   | tan d | E'   | tan d |
| 6   | 2000            | 200  | 0.27  | 18   | 0.42  |
| 9   | 3300            | 250  | 0.25  | 60   | 0.25  |

E' - storage modulus, MPa; tan d - ratio between loss and storage moduli

# DMA data - E', tan d

for PUD's made with BA of different molecular weight

Blocking and heat resistance is better when storage modulus (hardness) is higher and loss modulus is lower (cohesive strength).

In other words, better heat and blocking resistance should be expected for polymers showing higher storage modulus and lower tan d at the temperature of interest.

| P | U <sup>PUD with</sup><br>D <sup>BD/A MWt.</sup> | 40°C |       | 50°C |       |
|---|---|------|-------|------|-------|
|   |   | E'   | tan d | E'   | tan d |
| 6 | 2000  | 200  | 0.27  | 18   | 0.42  |
| 9 | 3300  | 250  | 0.25  | 60   | 0.25  |

E' - storage modulus, MPa; tan d - ratio between loss and storage moduli

# Exceptionally hard coatings

## Effect of polyol $T_m$ and $T_g$ on surface hardness

- ? Common polyols for PUD - relatively low glass transition temperatures ( -20 to -40°C range). Novel PUDs with higher  $T_g$  provides higher hardness
- ? PUD's prepared with TMXDI and :
  - Neopentylglycol polycarbonate diol (Oxymer N112, ),  $T_m = 105^\circ\text{C}$
  - Cyclohexane/hexanediol polycarbonate diol ( Eternacoll UC 100 ,  $T_m = 54^\circ\text{C}$
- ? no solvent (or minimal amount of coalescing aid of your choice – not NMP!)
- ? film formation at ambient temperature
- ? extremely high surface hardness without crosslinking – 150-200 sec (König)

# Relation between storage modulus $T_g$ , ( $E'$ ) and hardness

| PUD | Polyol          | $T_g$ (by DSC) |               | $E'$ , MPa @ 20°C | König hardness, sec |          |
|-----|-----------------|----------------|---------------|-------------------|---------------------|----------|
|     |                 | Polyol         | Poly-urethane |                   | RT (a)              | 120° (b) |
| 15  | HAT             | -39            | -14           | 400               | 43                  | 45       |
| 19  | NPG-carb        | 16             | 20            | 1800              | 83                  | 129      |
| 20  | CHDM/H-carb 1/1 | -32            | 14            | 1300              | 60                  | 80       |
| 21  | CHDM/H-carb 3/1 | -15            | 26            | 1900              | 140                 | 187      |
| 22  | CHDM-carb       | 3              | 43            | 2100              | 95                  | 220      |

(a) - film dried at RT  
 (b) - film dried at RT and then annealed at 120°/30 min

# Elastic films/Soft coatings

made with TMXDI and highly viscous amorphous polyols

- ? Preparation without the use of a solvent or plasticizer.
- ? PUD gives very elastic films that have very high elongation at break and very low modulus

| Property   |     |     | at break |
|--|-----|-----|----------|
| elongation, %  | 100 | 500 | 800      |
| stress, psi  | 140 | 340 | 3300     |
| dumbbell specimen, 0.25" × 1" test area, thickness 5.2 mill; tested at 20 in/min separation rate |     |     |          |

- Tg at about -15°C and no apparent melting peak.
- Storage modulus comes to a rubbery plateau at 30-90°C,

Rubber-like PUD films/coatings co=solvent free

# Conclusions:

- ? Tertiary diisocyanate (TMXDI) is very useful for PUD preparation without use of any solvent when higher molecular weight or high-melting polyols are used. Hence, range of polyols useful for PUD preparation is considerably expanded.
- ? Polyols with higher molecular weight and high melting point are useful for achieving improved heat and blocking resistance in heat-sealable coatings.
- ? Polyols with high glass transition temperature provide PUD for coatings with significantly higher surface hardness.
- ? PUD's made with viscous amorphous polyols produce exceptionally soft coatings and highly elastic films.