Synthesis and Applications of Functional Polyurethane

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1. Water-borne Polyurethane

• Requirement
  – Green Round
  – VOC
  – Nonflammability
  – Non Toxic Operation Environment
1) Particle size vs. DMPA content

- Polyol : PTMG 2000
- Isophorondiisocyanate (IPDI)
- Chain extender : ethylenediamine

- Particle size depend on DMPA content
- 6 wt% of DMPA content:
  Critical particle size (50 – 60 nm)

Figure 1. Comparison of NCO–PPD with its chain extended PUD
2) Particle size vs. polyol

- PBEAG 2000, PTMG 2000
- Isophorondiisocyanate (IPDI)
- Chain extender: ethylenediamine
- DMPA content ↑: Particle size ↓

- Size of Ester type PUD < Ether type PUD
- Critical DMPA content: 6 wt% (50–60 nm)

Figure 2. Particle size variation with DMPA content and polyol types
3) Particle size vs. polyol mixing ratio

Fig. 3. Particle size of PUD with PTMG contents at 2wt% DMPA content.

Fig. 4. Particle size of PUD with PTMG contents at 6wt% DMPA content.

- Particle size follows rule of mixture
- Two Tg are appeared

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4) Liquid type ionic diols (THPP–diol) (synthesis reaction)

**Chemical Structure:**

- **Solid**
- Poor solubility in DMF, NMP
- High cost
- Steric hindrance

- **Liquid**
- Good miscibility
- Low cost
- Sec.-hydroxy
- No-steric hindrance

**Synthesis Reaction:**

1,2,3-tri (2-hydroxypropoxy) propane

+ Phthalic anhydride or Maleic anhydride

**Figure 5. Structure of ionic diols**
5) Particle size vs. THPP diols

Prepolymer mixing process
- Polyol: PTMG 2000
- Isocyanate: H$_{12}$MDI
- Neutralizer: TEA
- Chain extender: EDA
- Solid content: 30 wt%

- Particle size decreased
- Critical Acid content decreased
  (4–5 wt%)
- Properties of THPP–PUs are similar to DMPA–PU

![Graph showing particle size vs. acid content for different diols.]

Figure 6

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6) Surface energy of PU films

- Owens and Wendt method
- Standard solvent: \( \text{H}_2\text{O}, \text{CH}_2\text{I}_2 \)

\[
\gamma_{LV} (1 + \cos \theta) = 2 \left[ \left( \gamma^d_S \right)^{1/2} \left( \gamma^d_{LV} \right)^{1/2} + \left( \gamma^p_S \right)^{1/2} \left( \gamma^p_{LV} \right)^{1/2} \right]
\]

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<tr>
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<th>( \gamma^d_{LV} )</th>
<th>( \gamma^p_{LV} )</th>
<th>( \gamma_{LV} ) (dyne/cm)</th>
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<td>( \text{H}_2\text{O} )</td>
<td>21.8</td>
<td>51</td>
<td>72.8</td>
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<tr>
<td>( \text{CH}_2\text{I}_2 )</td>
<td>50.8</td>
<td>-</td>
<td>50.8</td>
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- Higher energy than DMPA–PU
- Hydrophilicity of THPP–PU is higher than DMPA–PU
7) Mechanical properties of THPP–PU films

- Acid content 2.7% (DMPA 6wt%)
- Similar trend at 2.0, 1.3 % acid content

Figure 8

PUD–D : derived from DMPA
PUD–P : derived from PA
PUD–M : derived from MA

DMPA 2wt%
DMPA 4wt%
DMPA 6wt%
2. PU/Polyacrylate hybrid

- Polyurethane dispersion
  - Self-emulsifying
  - Elastomeric property
  - High cost

- Polyacrylate
  - Low cost
  - Emulsifier required

  - High dispersion stability
  - Medium cost
  - Good Mechanical/Thermal Properties
1) Process

- Factors of Monomer diffusion into PUD
  - Surface ionic charge barrier
  - PUD’s surface area
  - Solubility for water
2) Hybrid particle size vs. MMA content (PTMG–PUD)

- PTMG 2000
- H12MDI
- Chain extender: ethylenediamine
- Acryl monomer: MMA

- Particle size depend on DMPA content
- Particle size is independent on MMA content
- High DMPA content (8, 10 %): Particle size increased with MMA content (swelling with MMA monomer)

Fig. 10 The particle size of polyether type PU/PMMA hybrid with different DMPA contents.

- •: DMPA 2 wt%
- □: 4 wt%
- ▲: 6 wt%
- ▼: 8 wt%
- ◇: 10 wt%
3) Hybrid particle size vs. MMA content (PBEAG–PUD)

- PBEAG 2000
- H_{12}MDI
- Chain extender: ethylenediamine
- Acryl monomer: MMA

- Particle size is smaller than PTMG–PU
- Particle size depends on DMPA content
- High DMPA content: particle size increased with MMA content

![Graph showing particle size vs MMA content](image)

*Fig. 11. The particle size of polyester type PU/PMMA hybrid with different DMPA contents.*

- ○: DMPA 2 wt%  ■: 4 wt%  △: 6 wt%  ▽: 8 wt%  ◇: 10 wt%
4) Hybrid particle size distribution vs. monomer hydrophilicity

PUD
- Polyol : PBEAG 2000
- Isocyanate : H$_{12}$MDI
- Ionic diol : DMPA
- Chain extender : EDA
- DMPA content : 6 wt%
- Prepolymer mixing process

- Butylmethacrylate(BMA) Hybrid :
  - Broad size distribution at 35%
- Hydroxyethylmethacrylate(HEMA) Hybrid :
  - Bimodal size distribution over 20 %
5) Mechanical property of PU/MMA hybrid

PUD
- Polyol : PBEAG 2000
- Isocyanate : H_{12}MDI
- Ionic diol : DMPA
- Chain extender : EDA
- DMPA content : 6 wt%
- Prepolymer mixing process

- Modulus increased with MMA content
- Elongation decreased with MMA content

Fig. 13. Stress-strain curve of polyester type PU/PMMA hybrid with the MMA contents at 6 wt% of DMPA.

--- MMA 0 wt%  --- MMA 20 wt%  --- MMA 40 wt%