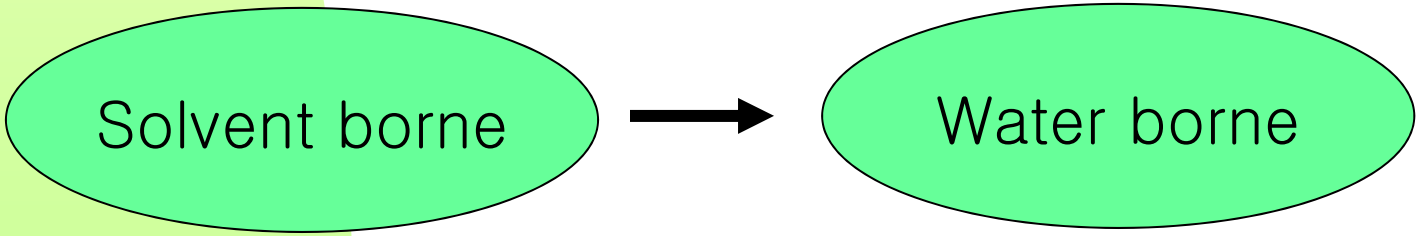
Synthesis and Applications of Functional Polyurethane

Noh Si Tae

Department of Chemical Engineering, Hanyang University

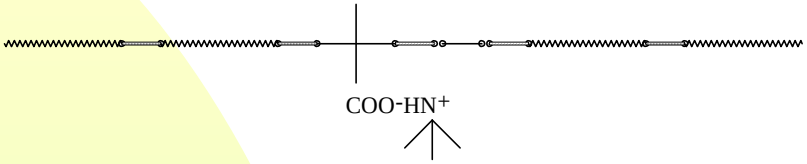
1.Water-borne Polyurethane

- Requirement
  - Green Round
  - VOC
  - Nonflammability
  - Non Toxic Operation Environment



1) Particle size vs. DMPA content

Anionic PU



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

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

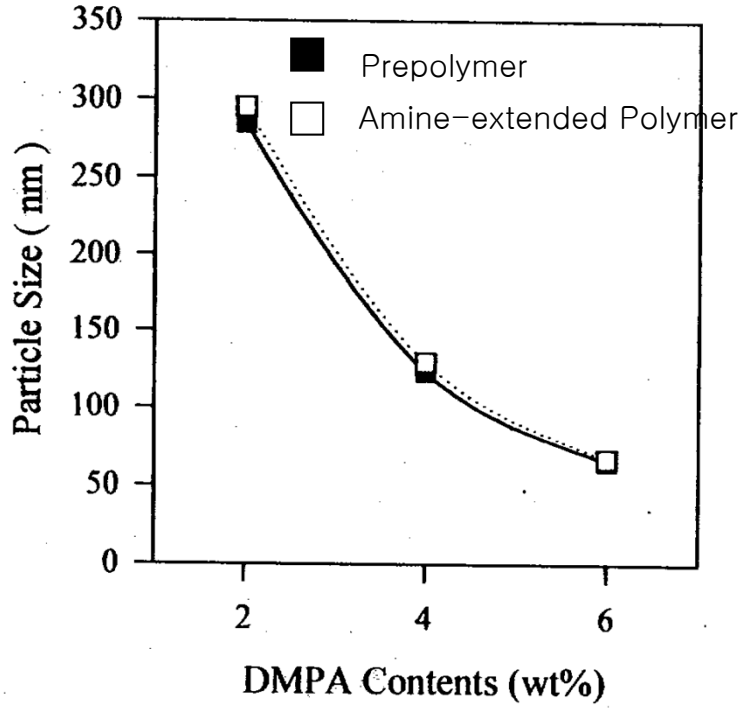


Figure 1. Comparison of NCO-PPD with its chain extended PUD

2) Particle size vs. polyol

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

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

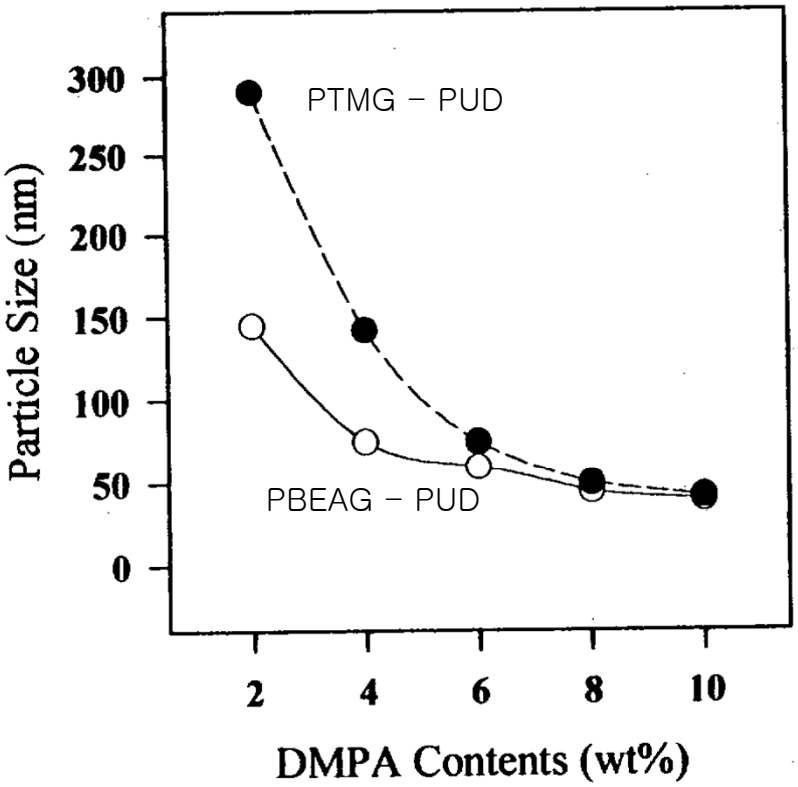


Figure 2. Particle size variation with DMPA content and polyol types

3) Particle size vs. polyol mixing ratio

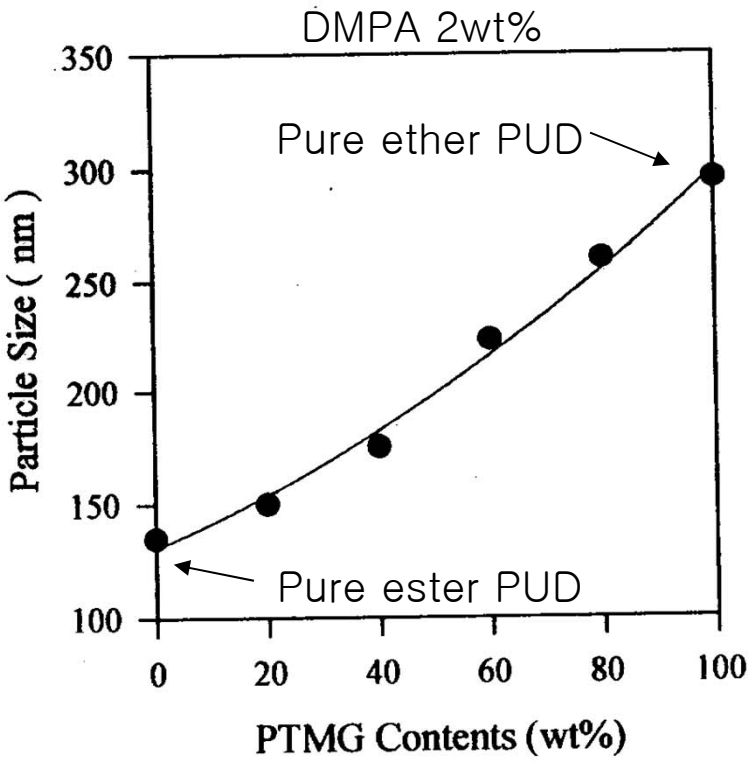


Fig. 3. Particle size of PUD with PTMG contents at 2wt% DMPA content.

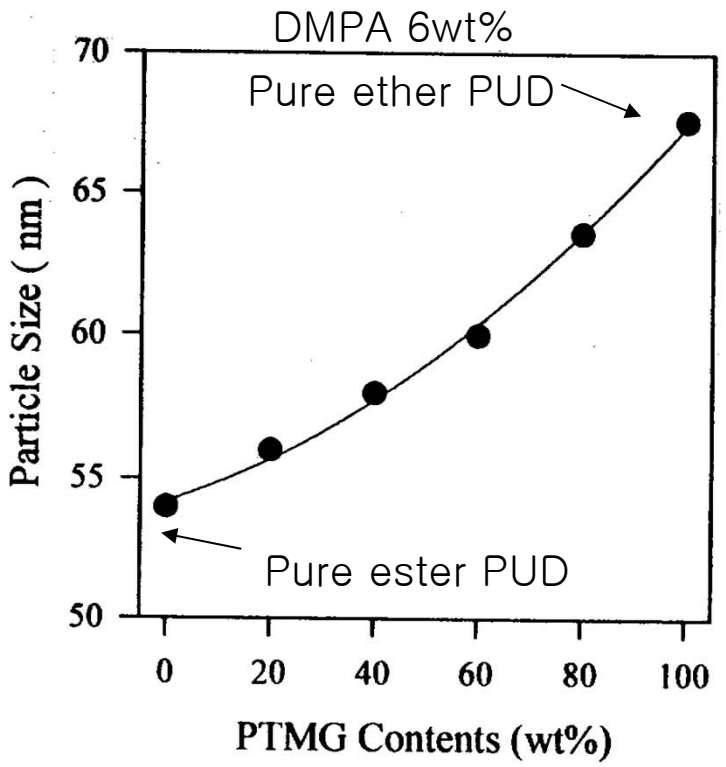
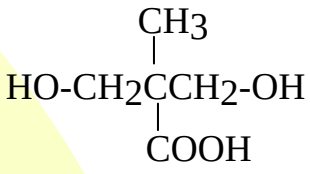


Fig. 4. Particle size of PUD with PTMG contents at 6wt% DMPA content.

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

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



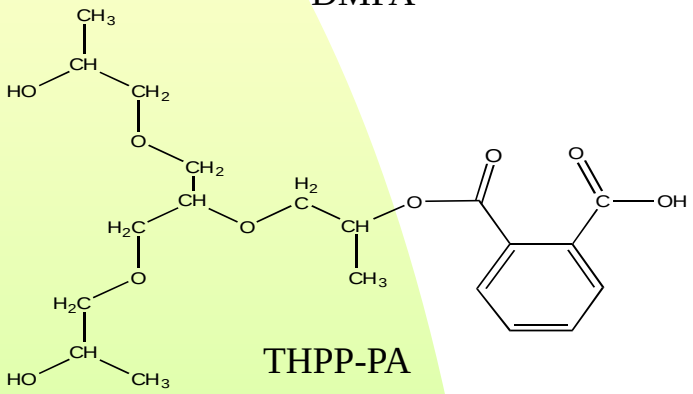
DMPA

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

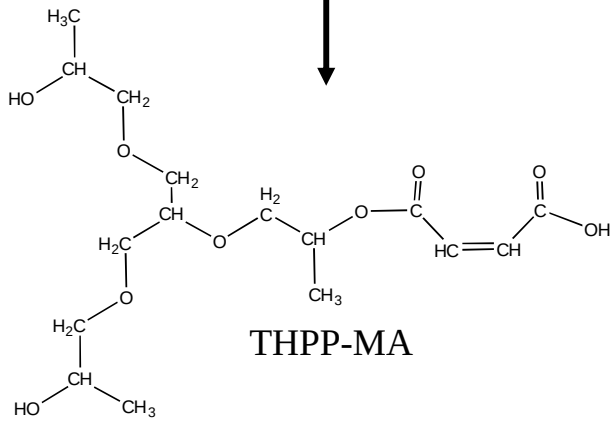
1,2,3-tri (2-hydroxypropoxy) propane

+

Phthalic anhydride or Maleic anhydride



THPP-PA



THPP-MA

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

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

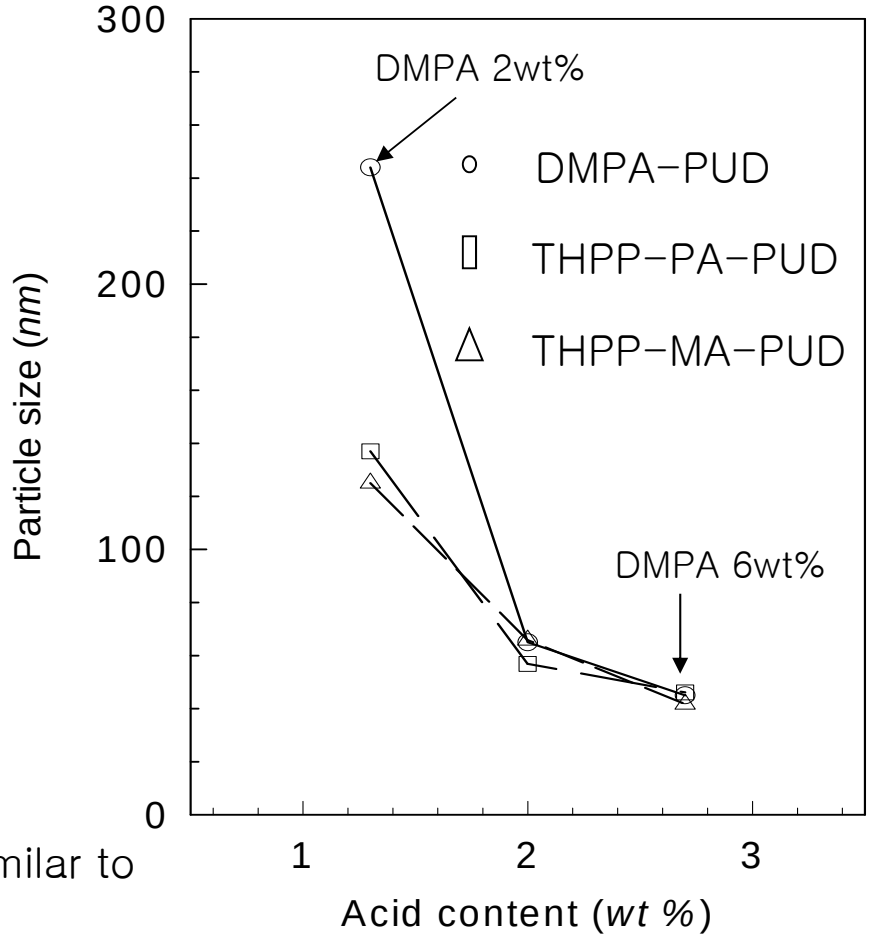


Figure 6

6) Surface energy of PU films

- Owens and Wendt method
- Standard solvent : H_2O, CH_2I_2

$$\gamma_{LV}(1+\cos\theta) = 2\left[\left(\gamma_S^d\right)^{1/2}\left(\gamma_{LV}^d\right)^{1/2} + \left(\gamma_S^p\right)^{1/2}\left(\gamma_{LV}^p\right)^{1/2}\right]$$

	γ_{LV}^d	γ_{LV}^p	γ_{LV} (dyne/cm)
H_2O	21.8	51	72.8
CH_2I_2	50.8	–	50.8

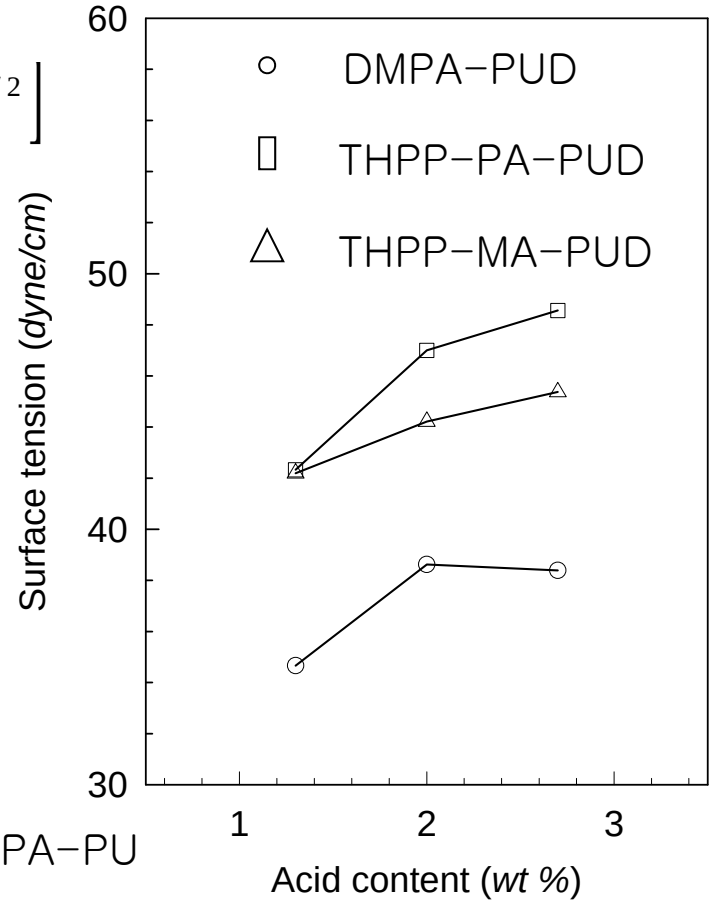


Figure 7

- 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%)
  - TMPP-PA-PU > DMPA-PU > THPP-MA-PU
- Similar trend at 2.0, 1.3 % acid content

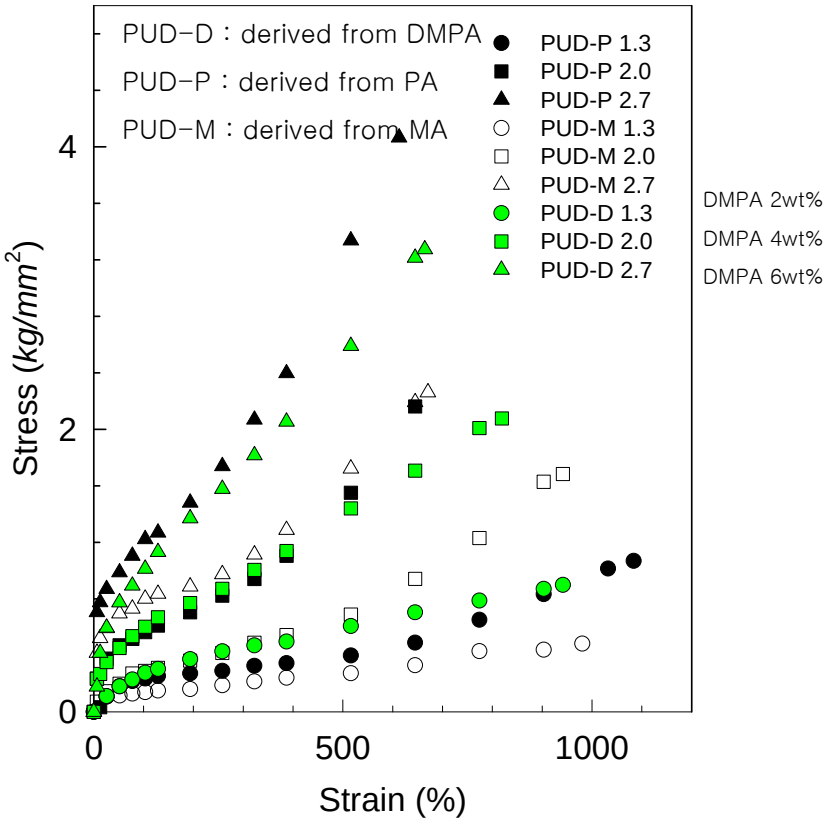


Figure 8

2. PU/Polyacrylate hybrid

- Polyurethane dispersion
  - Self-emulsifing
  - 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

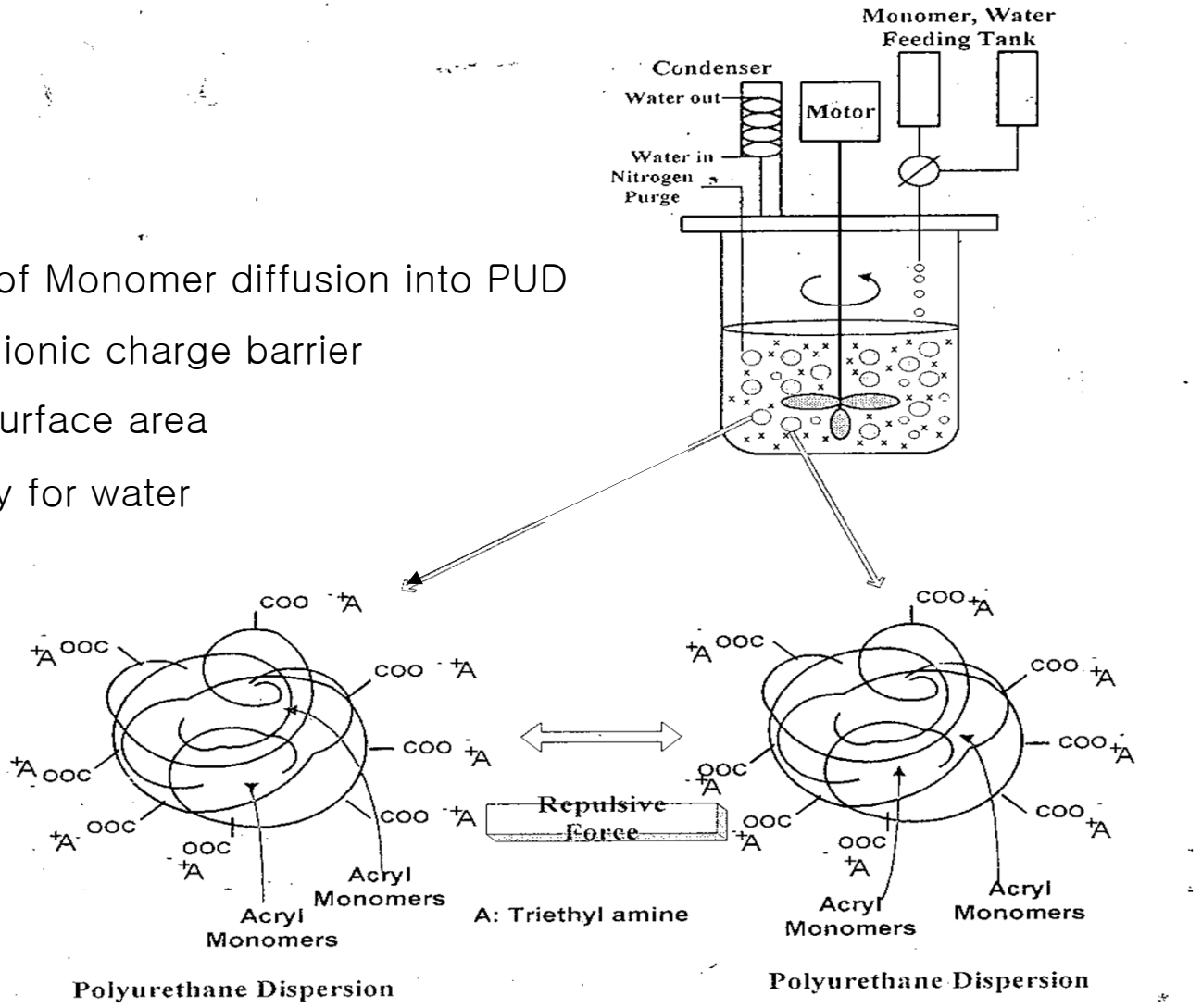


Figure 9

2) Hybrid particle size vs. MMA content (PTMG-PUD)

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

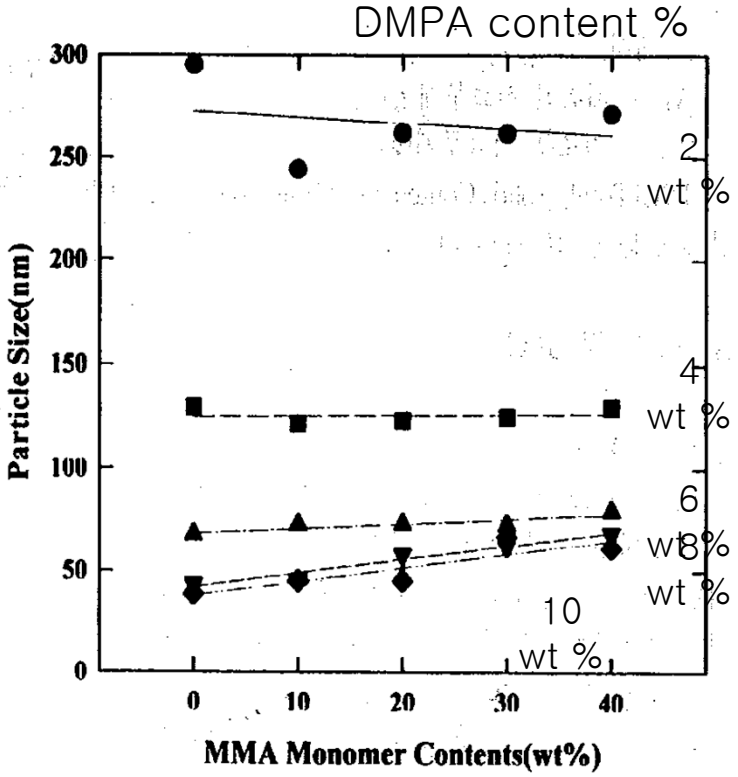


Fig. 10 The particle size of polyether type PU/PMMA hybrid with different DMPA contents.
-●- : DMPA 2 wt% -■- : 4 wt% -▲- : 6 wt%
-▼- : 8 wt% -◆- : 10 wt%

- 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)

3) Hybrid particle size vs. MMA content (PBEAG-PUD)

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

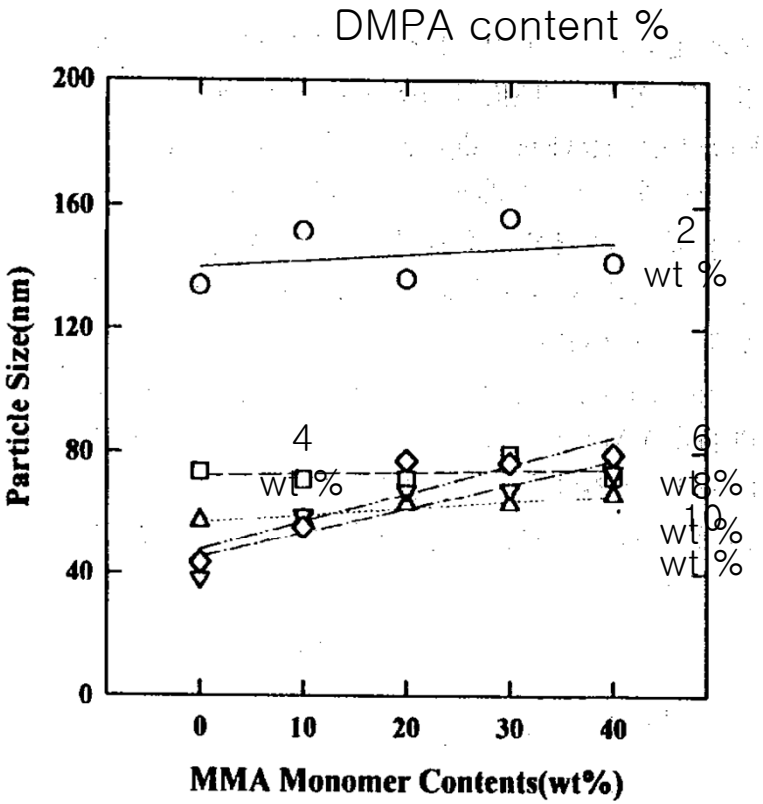


Fig. 11 The particle size of polyester type PU/PMMA hybrid with different DMPA contents.
-○- : DMPA 2 wt% -□- : 4 wt% -△- : 6 wt%
-▽- : 8 wt% -◇- : 10 wt%

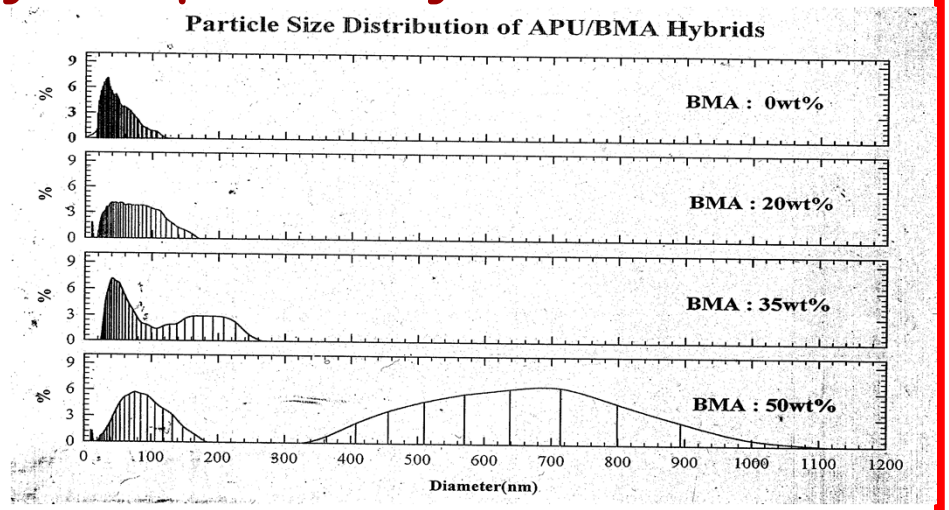
- Particle size is smaller than PTMG-PU
- Particle size depends on DMPA content
- High DMPA content :
  particle size increased with MMA content

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 %



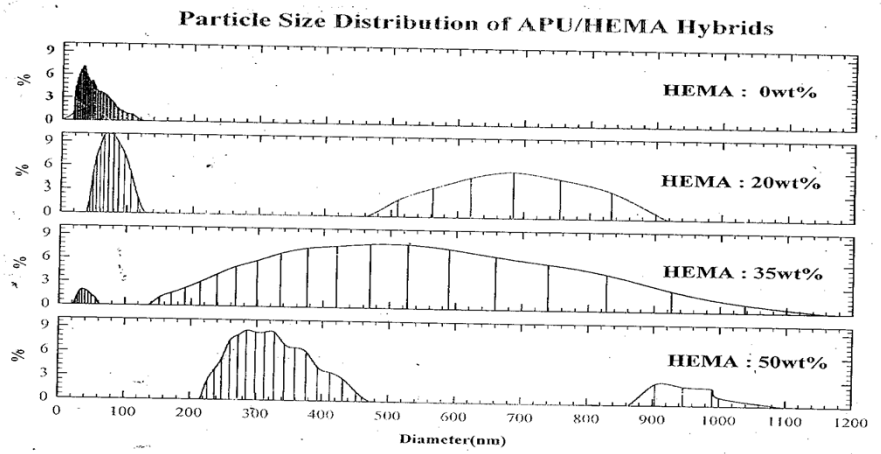


Figure 12

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

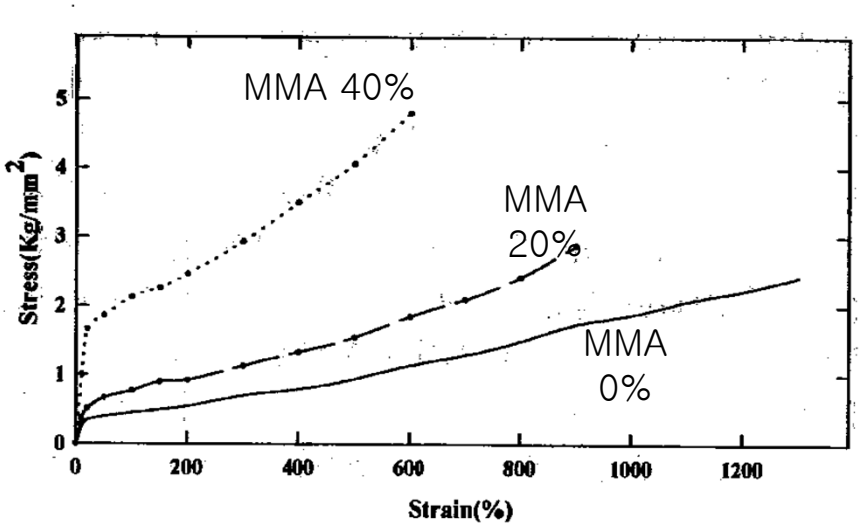


Fig. 13. Stress-strain curve of polyester type PU/PMMA hybrid with the MMA contents at 6 wt% of DMPA. – – : MMA 0 wt% –●– : MMA 20 wt% ···○··· : MMA 40 wt%