# Poly(ethylene glycol)을 이용한 수분산 폴리우레탄 hydrogels의 제조와 물성
## -EDA 및 DMPA 함량의 영향-

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# Preparation and Properties of Waterborne Polyurethane-Urea Hydrogels Based on Poly(ethylene glycol):
## -Effect of EDA and DMPA Content-

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## 1. Introduction

Over the last 30 years, water-swellable and water-insoluble hydrogels have been extensively investigated and developed, leading to a large family of materials which have found use in a wide range of biomedical applications such as carriers of soft tissues, wound healing, ophthalmological applications, membranes for artificial kidney, and materials for blood compatible and other medical devices[1-3].

While hydrogels usually present a crosslinked structure, linear polyurethane-ureas (PUUs) based on poly(ethylene glycol) have been shown to be able to absorb and swell with aqueous media without dissolving[4-7]. This behavior is due to the phase separated domain morphology, where strongly hydrogen bonded urethane-urea hard segment domains are dispersed in a PEO soft segment domain. As a result of their linear structure, the PUU hydrogels are soluble in organic solvents (e.g. methanol, ethanol, MEK) and devices and coatings can be fabricated using solvent casting techniques. The PUU hydrogels may also be processed using common thermoplastic fabrication techniques such as extrusion and injection molding.

In this study, waterborne polyurethane hydrogels were prepared by polyaddition reaction using poly(ethylene glycol) (PEG, MW=2000) as a soft segment, biscyclohexylmethane4,4-diisocynate ($H_{12}$MDI) as a hard segment, dimethyol propionic acid (DMPA), triethylamine (TEA) as a neutralization agent, and ethylene diamine (EDA) as a chian extender. This reseach has beenfocused on the effect of NCO/OH mole ratio and DMPA content with a fixed molecular weight (MW=2000) of PEG on the properties hydrogel, hardness and thermal properties.

## 2. Experimental

### 2.1. Materials

Poly(ethylene glycol) (PEG, MW=2000, Korea Polyol) was dried under vacuum at 95℃ for 3 hours on a rotary evaporator and was molten in an oven at 80℃. Biscyclohexylmethane 4,4-diisocyanate ($H_{12}$MDI, Aldrich Chemical), dimethyol propionic acid (DMPA, Aldrich Chemical),

triethylamine (TEA, Junsei Chemical), ethylene diamine (EDA, Junsei Chemical), N-methyl-2 pyrrolidone (NMP, Junsei Chemical), and dibutyl tindilaurate (DBTDL, Aldrich Chemical) were used without further purification.

**2.2 Synthesis of the waterborne polyurethane hydrogels**

A 500ml round-bottom 4-necked separable flask with a mechanical stirrer thermometer, condenser with drying tube, and a pipette outlet was used as reactor.
Reaction was carried out in a constant temperature oil bath with ±1℃ precision. PEG, DMPA, NMP, and DBTDL were charged into the dried flask, while stirring the mixture was heated to 80℃ for about 30 min. Homogeneized mixture was let down at 45℃, then $H_{12}$MDI was added. The mixture was heated to 85℃ for about 3hrs to obtain NCO terminated prepolymer. The change of NCO value during the reaction was determined using standard dibuthylamine back titration upon obtaining the theoretical NCO value. The temperature of the prepolymer had been cooled down at 50℃. It had been added TEA neutralizing solution for 30min at 40℃. After then, demineralized water had to add in this solution in order to foam dispersion. EDA solution dissolved in water were fed in the emulsion every 3min for 2 hours. The final product was a stable and the solid content of waterborne polyurethane-urea hydrogel was controlled to about 40%.

**2-3 Characterization**

FT-IR (Nicolet impact 400D) spectrometer was used to identify the structure of waterborne polyurethane hydrogels. The thermal property of sample was examined by using a DSC 220C (SEIKO) at a heating rate of 10℃/min under a nitrogen atmosphere. Thermal gravimetric analysis of film was carried out using TGA (TA instrument) at a heating rate of 20℃/min over a temperature range of 30℃ ~ 600℃. Hardness (Shore F type) and repulsion force (Asker Ball Rebound Test) were measured at 25℃, 35℃, 45℃, and 50℃, respectively.

**3. Results and Discussion**

Waterborne polyurethane hydrogels were prepared by polyaddition reaction using $H_{12}$MDI, PEG, DMPA, TEA and EDA. Sample designation and composition of waterborne polyurethane hydrogels synthesized in this study are shown in Table 1. The hardness and repulsion force of the gel sample increased with increasing chain extender EDA and DMPA contents. The hardness and repulsion force of gels were significantly depended on the temperature.

**4. References**


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Table 1. Sample designation and composition of waterborne polyurethane hydrogels

| Sample designation | Composition (Molar ratio) | | | | |
|---|---|---|---|---|---|
| | H12MDI | PEG | DMPA | EDA | TEA |
| HE-1 | 3.0 | 1.2 | 0.8 | 1.0 | 0.8 |
| HE-2 | 3.0 | 1.1 | 0.8 | 1.1 | 0.8 |
| HE-3 | 3.0 | 1.0 | 0.8 | 1.2 | 0.8 |
| HE-4 | 3.0 | 0.9 | 0.8 | 1.3 | 0.8 |
| HD-1 | 3.0 | 1.8 | 0.2 | 1.0 | 0.2 |
| HD-2 | 3.0 | 1.6 | 0.4 | 1.0 | 0.4 |
| HD-3 | 3.0 | 1.4 | 0.6 | 1.0 | 0.6 |
| HD-4 | 3.0 | 1.2 | 0.8 | 1.0 | 0.8 |
| HD-5 | 3.0 | 1.0 | 1.0 | 1.0 | 1.0 |

Table 2. Physical properties of waterborne polyurethane hydrogels

| Sample designation | Hardness (Shore F type) | | | | Repulsion force (Asker Ball Rebound Test) | | | |
|---|---|---|---|---|---|---|---|---|
| | (℃) | | | | | | | |
| | 25 | 35 | 45 | 50 | 25 | 35 | 45 | 50 |
| HE-1 | 45 | 35 | 20 | 13 | 25 | 15 | 12 | 10 |
| HE-2 | 55 | 37 | 25 | 22 | 29 | 20 | 15 | 13 |
| HE-3 | 60 | 43 | 27 | 25 | 33 | 21 | 16 | 14 |
| HE-4 | 68 | 45 | 28 | 26 | 36 | 22 | 16 | 14 |
| HD-1 | 35 | 20 | 14 | 10 | 17 | 13 | 9 | 7 |
| HD-2 | 38 | 22 | 16 | 12 | 18 | 14 | 10 | 8 |
| HD-3 | 60 | 40 | 27 | 24 | 30 | 21 | 17 | 14 |
| HD-4 | 62 | 44 | 34 | 25 | 34 | 25 | 19 | 17 |
| HD-5 | 64 | 48 | 36 | 30 | 36 | 28 | 20 | 19 |