

투습성 수분산 폴리우레탄의 제조와 특성

- 폴리올의 영향 -

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Preparation and Properties of Water Vapor Permeable Waterborne Polyurethane

-Effect of Polyol-

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1. Introduction

Waterborne Polyurethane dispersions continue to show growth in commercial usage due to the ever increasing environmental legislation to reduce VOC in Coating and adhesive materials. The transition from solvent-based to waterborne Polyurethane(WPu) has also been facilitated by advances in both the chemistry and technology employed and the formulation expertise required.

The physical properties of Polyurethane(Pu) is significantly affected by the composition of the soft segments. In general, the ester type polydiol-based Pu displays better mechanical properties, whereas the ether type Pu displays better hydrolysis, softness, and water-vapor permeability(WVP). To improve the physical properties, a mixed or special type of polyol as soft segment of Pu was used for imparting Pu with specific properties. Xiu et al.¹⁾ used ester-ether copolydiol(Polypropylene oxide and maleic anhydride) as mixed soft segments to study the influence of soft segment structure and molecular weight on the physical properties of Pu film. Polyester-ether based Pu displayed a higher Young's modulus and lower elongation than polyester-based or polyether-based Pu, primarily due to the larger interface within domains. Cooper et al.²⁾ used poly(dimethyl siloxane)(PDMS) and Poly(tetramethylene glycol)(PTMG) as mixed soft segments and found that the Pu had better water absorption and moisture sensitivity than Pu with PDMS as the soft segment. Yen et al.³⁾ was studied on the effects of the soft segment composition on the structure and physical

properties of synthesized WPu by using the PCL-PEG-PCL triblock copolydiol as the soft segment and found that WVP increased as the SSC increased.

In this study, waterborne polyurethane with types of single, mixture and triblock polyol(TBG) as a polyol was prepared from the reaction of isophorone diisocyanate(IPDI) with various polyol, DMPA as an ionic moiety, ethylene diamine(EDA) as a chain extender and proceeded neutralizing agent of pendant COOH groups by triethylamine(TEA) as a neutralization. The effects of types of single, mixture and triblock polyol(TBG) as a polyol in the waterborne polyurethane were investigated.

2. Experimental

2.1. Materials

The materials used in this study are summarized in Table II. Monomer CL(Sigma) and PTMG(Aldrich) was dried over calcium hydride at room temperature for 24 hours, then distilled under reduced pressure(b.p 96°C/15mmHg) before use. Dimethylol propionic acid(DMPA), Polycaprolactone(PCL), Polypropyleneglycol(PPG), Polytetramethylene adipate(PTAd) and Polydimethylsiloxanpolyoxyethylene(PSiG, Dow corning) was dried in a vacuum oven(100°C) for at least 5 hours. Isocyanate(IPDI), Ethylene diamine(EDA, Aldrich), Triethylamine (TEA, KASEI), MEK, N-methyl-2 pyrrolidone(NMP, Aldrich), Dibutyl tin dilaurate(DBTDL, Aldrich) were used without further purification

2.2. Synthesis

2.2.1. Synthesis of triblock polyol(TBG, PCL-PTMG-PCL): The reaction proceeded under nitrogen protection in a four neck round bottomed flask equipped with a thermometer, stirrer, inlet of dry nitrogen, condenser and a heat jacket. PTMG($M_n=1000$)(50g) was reacted with the stoichiometric amount of caprolactone(CL)(51g) at 180°C for 48 hours. Then the reaction mixture were vacuum distilled to remove the unreacted CL at 190°C. TBG obtained was dried in a vacuum oven at 100°C for a week.

2.2.2. Synthesis of waterborne polyurethane: The composition of waterborne polyurethane is show in Table II. The segmented prepolymer used in this study was synthesized by a one step addition reaction. Isophorone diisocyanate(IPDI) was charged under a nitrogen gas atmosphere, and a solution of polyol and DMPA/NMP(2.35g/6g) with DBTDL catalyst was then added slowly over a period of 1h under gentle stirring(150rpm). The mixture was allowed to react at 80°C until the theoretical NCO content were reached as determined by the di-n butylamine titration method. The NCO-terminated Pu prepolymer solution were

adjusted to addition of a suitable amount of MEK(18%). Triethylamine as a neutralizing agent was added to the freshly prepared NCO-terminated Pu prepolymer solution. After 30min, distilled water was added to Pu prepolymer. Ethylene diamine as a chain extender in aqueous solution was added to the NCO-terminated Pu prepolymer solution. An aqueous dispersion of ca. 30wt% solids was obtained upon removal of acetone by rotary vacuum evaporation.

2.3 Characterization

Particle size analysis was done using light-scattering equipment (Autosizer, Melvern IIC). A few drops of the dispersion were diluted in non-ionized water before the measurement. The viscosity of waterborne polyurethane dispersions was measured using a Brookfield digital viscometer, Model DV-II+ at 20°C. FT-IR spectra were collected using a Nicolet impact 400D at resolution of 4cm^{-1} , and 32 scans was signal-averaged at room temperature. Tensile properties were measured at room temperature using a Untied Data System (Instron, SSTM-1) tensometer following the ASTM D-412 specification. A crosshead speed of 50mm/min was used throughout these investigations to determine the tensile strength and elongation at break for all the samples. The values quoted are the average of four or five tests.

3. Results and Discussion

Molecular weight of triblock polyol(TBG) synthesized in this study was 1990. The triblock polyol(TBG) was identified using FT-IR spectra and DSC measurement (see Figure 1). The characteristics of TBG are shown in Table I. The molecular weight of TBG was found to be 1990. Infra-red spectrum of triblock polyol revealed the presence of hydroxyl end groups and carbonyl groups. From DSC curve, it was found that the triblock polyol has two melting peaks.

Waterborne polyurethanes were prepared from IPDI/EDA/DMPA/TEA/single(or mixture) of various polyols. The polyols used in this study were TBG synthesized here, polydimethylsiloxaneoxyethylene polyol (PSiG, $M_n=600$), PPG($M_n=2,000$), PTMG($M_n=2,000$), PTAd($M_n=2,000$) and PCL($M_n=2,000$). Particle size of waterborne polyurethane prepared here was in the range of 10nm to 60nm. The viscosity of PSiG/TBG based waterborne polyurethane were significantly increased with increasing PSiG content of PSiG/TBG. However, their tensile properties were almost not changed with PSiG content from 1.1 to 3.3 wt%.The polyurethane film containing PTAd had the best tensile strength and the lowest elongation (see Table II)

4. References

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Table I. The characteristics of triblock polyol(TBG)

Sample	Mn(Theory)	Mn(HVT)*	Yield(%)	Tm(°C)	
Triblock copolydiol	2000	1990	95	13	40

*Mn(HVT) was determined from hydroxyl value ($Mn=56.11 \times 2000/OH.V$).

Table II. Formulation details and properties of the waterborne polyurethanes prepared in this study

Sample	IPDI	Polyol (Mn=2000)		DMPA	EDA	TEA	Viscosity (cPS) ^{a)}	Tensile stregth (Kgf/cm ²)	Elongation (%)
H-PPG	3	1.2		0.8	1	0.8	34.3	15	1631
H-PTAd	3	1.2		0.8	1	0.8	13.8	165	918
B-PCL:PPG	3	0.6	0.6	0.8	1	0.8	16.7	8.37	1042
B-PCL:PTMG	3	0.6	0.6	0.8	1	0.8	12	38	1128
B-PTAd:PPG	3	0.6	0.6	0.8	1	0.8	10.9	68	1128
B-PTAd:PTMG	3	0.6	0.6	0.8	1	0.8	10	254	1137
T-TBG	3	1.2		0.8	1	0.8	8.1	3.84	2500
T-PSiG1.1	3	1.2		0.8	1	0.8	8.9	3.82	2527
T-PSiG2.2	3	1.2		0.8	1	0.8	15.1	3.83	2523
T-PSiG3.3	3	1.2		0.8	1	0.8	58	4.9	2628

a) Viscosity of Waterborne Polyurethane at 25°C (spindle 1, Solids 30wt%)

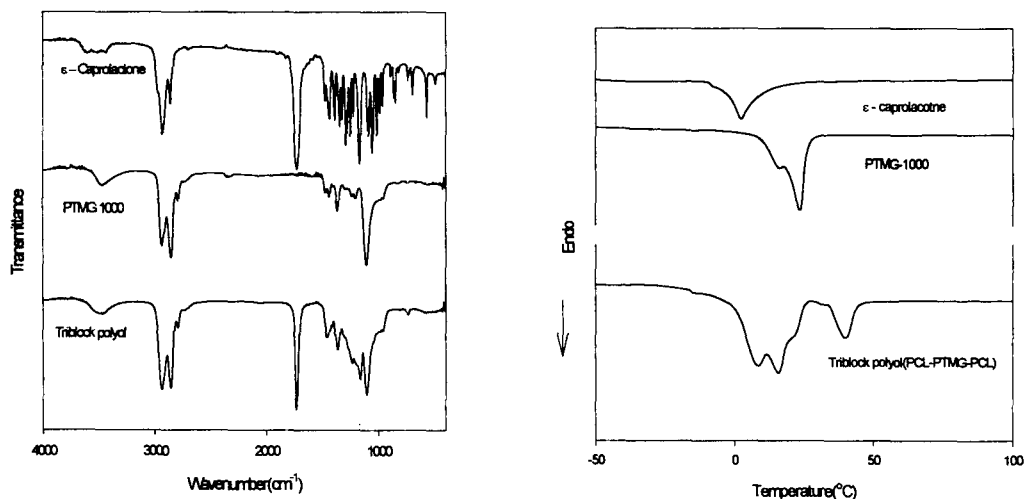


Figure 1. IR-Spectra and DSC curve of CL, PTMG and triblock polyol(TBG)