

수분산 폴리우레탄의 제조 및 특성 - DMPA 함량의 영향 -

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Preparation and Properties of Waterborne Polyurethanes - Effect of DMPA content -

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1. Introduction

Polyurethane are used for a wide range of commercial applications such as adhesives or coatings for various substrates including textile fabric, plastic, wood, glass fiber, and metals. The types of polyurethane ionomers have been reported according to the ionic charges on the polymer main chain, i.e. anionomer¹⁾, cationomer²⁾, and zwitterconomers³⁾.

Ionomers contain a certain number (usually 10mol% or less) of inorganic salt groups attached to a polymer chain. Ionization has a strong effect on many of their physical properties. Even small amounts of ionic groups can sufficiently modify specific properties of materials. Ionization causes improved adhesive, toughness, tear strength, and abrasion resistance. The presence of the ionic species in PU ionomers has a considerable effect on the physical properties, and it is reasonable for these effects.

One of the most important characteristic of many polyurethane ionomer is their ability to disperse or dissolve in water if a sufficient amount of ionic moiety is incorporated.

In the article, we study the effect of DMPA content on the stability and viscosity of aqueous dispersion, and adhesives strength.

2. Experimental

2.1. Materials

Poly(tetramethylene adipate) glycol (PTAd, Mw=2000, Hosung Chem.) was dried

at 100°C, 1-2 mmHg for at least 5 hrs before use. Other extra grades of Dimethylolpropionic acid (DMPA, Aldrich), Triethylamine (TEA, Junsei), N-methyl-2-pyrrolidone (NMP, Junsei), Isophrone diisocyanate (IPDI, Huls AG) Ethylene diamine (EDA, Junsei) and Dibuthy-tin-dilaurate (DBTDL, Aldrich) were used without further purification.

2.2. Synthesis of the waterborne Polyurethane-Urea

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 $\pm 1^\circ\text{C}$ precision. PTAd, DMPA, NMP, and DBTDL were charged into the dried flask while stirring the mixture was heated to 80°C for about 30 min. Homogenized mixture was cooled to 50°C, then IPDI was added. The mixture was heated to 85°C for about 4hrs to obtain NCO terminated prepolymers. The change of NCO value during the reaction was determined using standard dibuthyamine back titration upon obtaining the theoretical NCO value, the prepolymers were cooled to 50°C, and TEA neutralizing solution was added and stirred 30min while the temperature was maintained at 40°C while stirring rapidly, demineralized water was added to the solution to foam dispersion EDA solution dissolve in water were then fed to the emulsion for a period of 30 min, and chain extension was carried out for the next 2hrs. the resulting product was a stable, at room temperature, urethane-urea dispersion with a solid content about 39-40%.

2.3. Characterization

Particle size of the dispersion was measured using light-scattering equipment(Autosizer Melvern.IIc). FT IR spectra were collected using a Nicolet impact 400D at resolution of 4cm⁻¹, and 32 scans were signal-averaged at room temperature. The thermal behavior of samples were examined by using a DSC 220C(Seiko) at a heating rate of 10°C/min under nitrogen atmosphere. Adhesive and Tensile properties were measured at room temperature using Untied Data System(Instron, SSTM-1) tensometer following the ASTM D-638 spcfication A crosshead speed of 100mm/min was used throughout these investigations to determine the ultimate tensile strength and elongation at break for all the samples The values quoted are the average of four tests.

3. Results and Discussion

Waterborne polyurethane anionomers were prepared by polyaddition reaction using IPDI, PTAd, DMPA, and ethylene diamine as a chain extender. Sample

designation and composition of waterborne polyurethane synthesized in this study are shown in Table I. Table II shows the stability viscosity of aqueous polyurethane dispersion, and adhesive test results. Aqueous dispersions of samples D-2.0 and D-2.5 were unstable and aqueous dispersion of sample D-3.0 was meta- stable, however, samples D-3.5, D-4.0 and D-4.5 were stable dispersion. The viscosity increased with increasing DMPA content (see Figure 1). Samples D-4.5 and D-5.0 were too viscose. Therefore, it was very difficult to obtain aqueous dispersion containing more than 40wt% of polymer solid when DMPA was used above 4.5g per polyol 100g. From these results, we found that DMPA 3.5-4.0g per polyol 100g was an optimum content to obtain good adhesives. Adhesive test was done using CR-rubber/CR-rubber, CR-rubber/polyurethane and CR-rubber/EVA as substrates, but the test was failed because substrate materials was broken. We found that all polyurethane samples prepared in this study have strong adhesive properties. Therefore, we are going to try adhesive test using another material as substrates.

4. References

1. H. A. Al-Salah, K. C. Frisch, H. X. Xiao, and A. Molean, *J. Polym., Sci., Part A Polym., Chem.*, **25**, 2127 (1987).
2. A. Rembaum, H. Rile, and R. Someano, *J. Polym., Sci.*, **138**, 457 (1970).
3. K. K. S. Hwang, C. Z. Yang, and S. L. Cooper, *Polym. Eng. Sci.*, **21**, 1027 (1981).
4. H. Chen, D. Chen, and Q. Fan, *J. Polym. Sci.*, **76**, 2049 (2000).

Table 1. Sample designation and composition of waterborne polyurethane (mole ratio)

Sample Designation	IPDI	PTAd ¹⁾	DMPA	EDA	TEA
D-2.0 ²⁾	0.30	0.17	0.05	0.08	0.05
D-2.5 ²⁾	0.31	0.17	0.06	0.08	0.06
D-3.0	0.32	0.17	0.07	0.08	0.07
D-3.5	0.33	0.17	0.08	0.08	0.08
D-4.0	0.34	0.17	0.09	0.08	0.09
D-4.5	0.35	0.17	0.10	0.08	0.10
D-5.0	0.36	0.17	0.11	0.08	0.11

1) MW : 2000

2) D-2.0 and D-2.5 samples happened phase separation.

Table 2. Stability of Aqueous Polyurethane Dispersions and Adhesive Test Results

Sample Designation	Adhesive strength(kgf/cm)			Stability ⁴⁾
	R/R ¹⁾	R/PU ²⁾	R/EVA ³⁾	
D-2.0	-	-	-	X
D-2.5	-	-	-	X
D-3.0	7.7	7.7	2.9	△
D-3.5	7.8	7.8	3.0	○
D-4.0	7.9	7.8	3.1	○
D-4.5	7.8	7.8	3.0	○
D-5.0	7.8	8.0	3.1	○

1) : Rubber/Rubber

2) : Rubber/PU foam(Hardness A type 60)

3) : Rubber/EVA foam(Hardness A type 50)

4) X is unstable, △ is meta-stable, and ○ is stable.

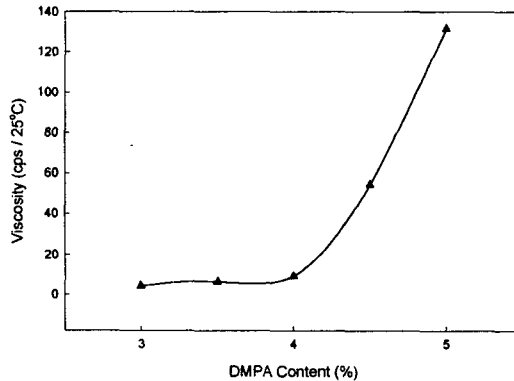


Figure 1. Effect of DMPA Content on Viscosity.