

〈研究論文(學術)〉

Soft Segment 길이가 Polyurethane Ionomer의 분산특성 및 물리적 특성에 미치는 영향

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Effect of Soft Segment Length on the Dispersion and Physical Properties of Polyurethane Ionomer

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요 약—IPDI, PTAd 및 DMPA(음이온 중심)를 사용하여 폴리우레탄 아이오노머를 합성하고 여기에 물을 첨가하여 수분산 폴리우레탄을 제조하였다. 폴리올 분자량(Mn)이 분산상태 및 에멀전 주사 필름의 열적, 기계적, 점탄성적 성질 및 팽윤에 미치는 영향을 측정하였다. 폴리올 분자량이 증가할수록 에멀전 입경과 soft segment T_g 는 감소하였으며, 용매팽윤, 에멀전 점도, hard segment T_g 는 증가하였다. 필름의 인장강도는 Mn=1000에서 최소치를 나타냈으며, 파단 신율은 폴리올 분자량 증가와 더불어 증가하였는데 이러한 결과는 soft-hard segment 상분리와 고분자량 PTAd의 결정화로 적절히 설명할 수 있었다.

1. ABSTRACT

Aqueous polyurethane(PU) anionomer dispersions were prepared from isophorone diisocyanate (IPDI), polytetramethylene adipate glycol(PTAd) and dimethylol propionic acid(DMPA) as potential anionic centers. The effects of polyol molecular weight(Mn) on the state of dispersion, thermal, mechanical, and viscoelastic properties and swelling of emulsion cast film were determined. With increasing Mn of PTAd, particle size of emulsion and soft segment T_g decreased, and solvent swell, emulsion viscosity, and hard segment T_g increased. Tensile strength showed minimum with PTAd 1000, and elongation at break generally increased with the Mn of PTAd. These results

were possibly interpreted in terms of soft segment-hard segment phase separation and crystallization of high molecular weight PTAd.

2. INTRODUCTION

Polyurethane(PU) ionomers are segmented copolymers which consist of alternating soft and hard segment units with a minority of repeat units carrying pendant acid or tertiary nitrogen groups which are neutralized to form salts. The soft segment generally consists of polyether or polyester polyol, whereas hard segments are usually formed by the extension of a diisocyanate with a chain extender of a low molecular polyol or amine.

It is now generally accepted that the properties of PU ionomers are primarily due to the phase behavior of soft and hard segments as well as ion character. The existence of the hard segment domain may particularly give PU ionomer an excellent mechanical strength.^{1,2)} An elevation in the soft segment glass transition temperature(T_g) is mostly observed as a result of the presence of a dissolved hard segment.^{3,4)} In general, the polyester soft segment was found to contribute phase mixing by hydrogen bonding between the oxygen of soft segment and NH groups of hard segment.^{5,6)} This behavior also depends on the content, length, and polarity of soft and hard segment. A large number of previous investigations^{7~11)} have reported on the characterization of this microdomain structure in segmented PU. However, with regard to PU aqueous dispersion most work was done by industrial laboratories, and basic structure/property behavior is sparse in the open literature.^{12~14)}

In this paper we describe the preparation and properties of PU ionomer dispersions from polytetramethylene adipate glycol(PTAd), isophorone diisocyanate(IPDI) and dimethylol propionic acid. The effect of soft segment molecular weight($M_n = 600 \sim 2000$) on the emulsion characteristics and properties of emulsion cast films were studied.

3. EXPERIMENTAL

3.1 Materials

PTAd(Dongsung Chemicals) was dried and degassed at 80°C, 1~2mmHg for 5h before use. DMPA(Aldrich) was dried at 100°C for 2h in drying oven. Extra pure grade of IPDI(Huls Chemicals) and dibutyltin dilaurate(DBT) were used as received. Dimethylformamide(DMF), triethylene tetramine(TETA), triethylamine(TEA), and solvents used in titration were dried over 3Å molecular sieve before use.

3.2 Prepolymer Synthesis

Basic formulation is given in Table 1. A 500ml round-bottom 4-necked separable flask with a mechanical stirrer, thermometer, condenser with drying tube, and a pipet outlet was used as reactor. Reaction was carried out in a constant temperature oil bath. PTAd, DBT(0.03 wt% based on the total solid weight), and DMPA dissolved in DMF(5 wt% based on the total weight) were charged into the dried flask. While stirring, the mixture was heated to 90°C for about 30m, followed by adding IPDI to the homogenized mixtures. The mixture was heated to 90°C for about 3h to obtain NCO terminated prepolymers. The change of NCO value during the reaction was determined using a standard dibutylamine back titration method.¹⁵⁾ Upon obtaining the theoretical NCO value, the prepolymers were cooled to 60°C, and the neutralizing solution, i. e., TEA dissolved in DMF(5 wt% based on the total weight) was added and stirred for 1h while maintaining the temperature at 60°C. The 1 : 1 stoichiometry was obtained by adding TETA at chain extension step. The amount of DMF used in each step, i. e., to dissolve the DMPA and to reduce the solution viscosity, was approximately the same(see the total amount in the tables).

Table 1. Basic Formulation of the Feed(unit : g)

Mn of PTAd	PTAd	DMPA	IPDI	TEA(ml)	TETA
600	18.6	1.93	12.45	2.0	1.18
1000	20.8	1.93	10.09	2.0	1.18
1500	22.2	1.93	8.68	2.0	1.18
2000	22.9	1.93	7.91	2.0	1.18

NMP : 300ppm, H₂O : 55g, DMF : 10ml

3.3 Emulsification and Chain Extension

Aqueous dispersion of PU was obtained by adding water(35°C) to the mixture(60°C). Since the

water addition rate, in addition to the viscosity ratio between prepolymer solution and water, is a critical parameter to obtain stable dispersion, a tubing pump was used, and water was added for 6m at a constant flow rate. The phenomenon of phase inversion, viscosity and conductivity change during the emulsification process are well documented in Dieterich¹⁶⁾ and our earlier papers.^{17, 18)} TETA dissolved in water was then fed to the emulsion for a period of 40m, and chain extension was carried out for the next 2h. The resulting product was a stable, over six months at room temperature, urea-urethane dispersion with a solid content of about 35%.

3.4 Tests

Particle size and its distribution were measured from Autosizer(Malvern II C), and state of dispersion was investigated from transmission electron microscopy(TEM, Hitachi H300). To obtain the micrographs, samples were stained with OsO₄ for 1 week. Tensile properties of the emulsion cast films were measured using an Instron Tensile Tester at a crosshead speed of 100mm/m, and an average of at least five measurements was taken to report. Films were prepared by casting the emulsion on a teflon plate, followed by drying at 80°C for 5h. The resulting films were then heated overnight in an oven at 60°C under 2~3mmHg. Microtensile test specimens were prepared according to ASTM D-1822. Dynamic mechanical tests were performed with a dynamic mechanical thermal analyser(DMTA, Polymer Lab.) from -100°C to 100°C at a frequency of 1Hz. To measure the swell in water and dimethylformamide(DMF), films were immersed in solvent for 24h at room temperature and, % swell was determined by measuring the weight increase via

$$\% \text{ swell} = \frac{\omega - \omega_0}{\omega_0} \times 100$$

where ω_0 is the weight of dried film and ω is the weight of film at equilibrium swell.

4. RESULTS AND DISCUSSION

4.1 Particle Size and Emulsion Viscosity

Throughout the experiments, the average molecular weight of NCO-terminated prepolymer was fixed at 4500. As the Mn of PTAd increases from 600 to 2000, hard segment content decreases from 48 to 38%. Table 2 shows that the particle size linearly decreases with increasing Mn of PTAd. The Autosizer result was visually confirmed from TEM(Fig. 1). In PU Dispersion, average particle size is mainly governed by the hydrophilicity of the PU.¹⁶⁻¹⁸⁾ However, the hydrophilicity marginally increases with increasing Mn of PTAd in the present system(to be shown later). The decrease of particle size with increasing Mn of PTAd has to be related with the increased chain flexibility of PU.

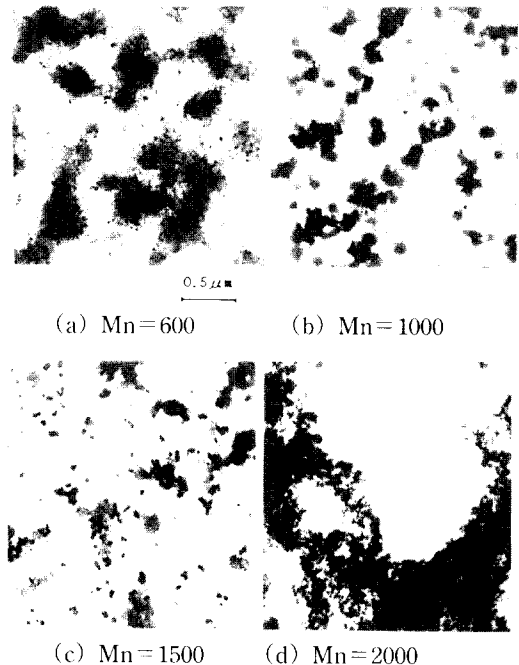


Figure 1. TEM micrographs for PU ionomer dispersions($\times 30,000$).

Table 2. Effect of the Mn of PTAd on Emulsion Characteristics and Film Properties

Mn of PTAd	Particle diameter (μm)	Emulsion viscosity (cPs, 20°C)	Hardness (Shore A)	Modulus(kg/cm ²)		Tensile strength (kg/cm ²)	Elongation at break(%)	% Swell(20°C)	
				200%*	300%*			Water	DMF
600	0.192	10.3	78.1	13.2	10.2	232	311	48	351
1000	0.126	10.8	79.0	20.1	11.3	203	321	57	612
1500	0.107	12.9	90.4	27.8	54.2	291	473	74	836
2000	0.048	42.0	92.2	9.3	7.8	325	582	92	1276

*200% : at 200% elongation

*300% : at 300% elongation

The effects of chain flexibility on the particle size reduction should be at least twofold. First, flexible particles are more deformable in shear field.^{19,20)} During the phase inversion, the dispersed phases are broken many times into smaller ones. Second, chain flexibility reduces the solution viscosity, which directly contributes to the fine breakup of the dispersed phase. Assuming stress continuity at interface, smaller dispersed phase viscosity leads to greater dispersed phase deformation according to²¹⁾

$$\eta_c \gamma_c = \eta_d \gamma_d$$

where η and γ are viscosity and rate of shear, and the subscripts "c" and "d" designate continuous and dispersed phase, respectively. These two contribute to the fine breakup of PU ionomer phase in water, leading to a smaller particle size. Conversely, when the particle size decrease is mainly caused by the increased hydrophilicity, an equilibrium particle size generally is obtained due to the increased swell of water at high hydrophilicity.

It is widely accepted that the ionic groups are predominantly located on the surfaces of particles and the ionomer dispersions are stabilized by the electrical double layers formation.^{1,2)} As the flexibility of PU chain increases with increasing soft segment content, the formation of micelle struc-

ture in water having the ionic sites on its surface will be more plausible. This augments the thickness of electrical double layers due to the effective structuring of the micelles, leading to the increased effective volume of dispersed phase of emulsion. The rate of water swell also increases as the particle size decreases due to the increased total surface area of the particles. In addition, at fixed total volume the effective hydrodynamic volume increases with decreasing particle size.²²⁾ These all contribute to the increased effective hydrodynamic volume of the dispersed phase, and the effect should be more pronounced with increasing chain flexibility, leading to a dramatic rise in viscosity with high Mn of PTAd.

4.2 Thermal Analysis

Figure 2 shows the DSC thermograms of PUs containing different Mn of PTAd. Generally the shorter the segments, the more compatible the hard and soft segments.²³⁾ Therefore soft segments prepared from higher Mn of PTAd are more likely to be phase separated with hard segments. With phase separated morphology, PTAd can be crystallized. Our DSC thermogram shows melting peak for PTAd 1500 and 2000. Among these two, soft segment crystallization is more perfect and the crystalline melting temperature is higher for PTAd 2000 than PTAd 1500. The increase of the

melting point is attributed to a increase in the size of the crystallites or an increase of complete crystalline phase due to the greater phase separation between the hard and soft segments.

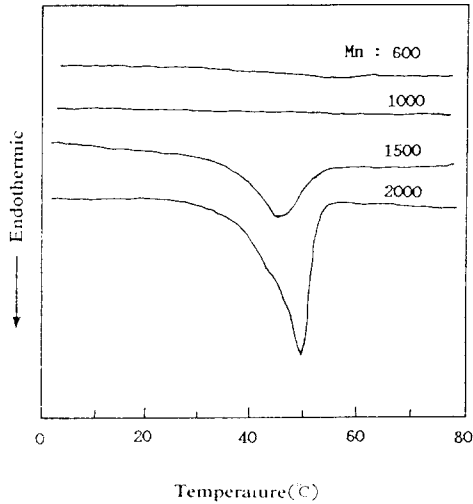


Figure 2. DSC thermograms of the emulsion cast films.

4.3 Viscoelastic Properties

The dynamic mechanical properties of the emulsion cast films as a function of temperature are shown in Figure 3. The storage moduli (E') (Fig. 3a) of PU from PTAd 600 and 1000 show behavior similar to the thermoplastic, whereas those from PTAd 1500 and 2000 show an upturn at about 0°C . The upturn, leading to higher value of E' at ambient temperature, should be related to the prevention of soft-hard phase mixing and soft segment crystallization.²⁰ When the phase mixing is relatively complete, the backbone mobility of soft segment is greatly restricted by the hard segments within the soft segments, and the hard segments are solubilized by the soft segments within the hard segments and lose their effectiveness as a filler or a physical crosslink.²⁰ The loss modulus (E'') peak (Fig. 3b) at $-25 \sim -35^{\circ}\text{C}$ corresponding to the T_g of the soft segment is

broader at lower Mn of PTAd especially at PTAd 600 and it moves toward the lower temperature as the Mn of PTAd increases. The decrease of soft segment T_g with increasing Mn of PTAd is due to the increased degree of soft-hard phase separation. A broad shoulder in PTAd 600 is an indication of intimate phase mixing, and the overall effect would be to hinder the motion of soft segments and broaden the distribution of their relaxation times.²³ The peak at about -85°C can be attributed to the relaxation process involving the local motion of methylene sequence of the polyester segment.^{12, 13}

The increased phase separation with increasing Mn of PTAd is again demonstrated in $\tan \delta$ curve (Fig. 3c). With the increase of Mn, lower peak (soft segment or soft segment-rich phase T_g) moves toward the lower temperature and higher peak (hard segment or hard segment-rich phase T_g) moves toward the higher temperature. Higher peak is defined for PTAd 600 and 1000 only, due to their relatively high hard content.

4.4 Mechanical Properties

Tensile strength and elongation at break (Table 2) show that a minimum strength is obtained with PTAd 1000. Basic structure-property relationship in PU states that hard segments affect hardness and strength, and are controlled by the total NCO content.²⁵ As the Mn of PTAd increases, less amount of hard segment and urethane linkage are formed to result in a decreased strength for PTAd 1000. As the Mn of PTAd further increases, soft-hard phase separation becomes evident and soft segments crystallize. These two factors, i. e., phase separation and soft segment crystallization, contribute to the strength.²⁶ The increase of elongation with Mn of PTAd primary comes from the augmented phase separations which provide PU with more perfect physical networks than in phase mixed morphology.²³

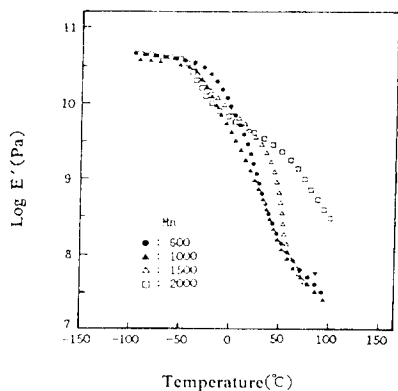


Figure 3. (a)

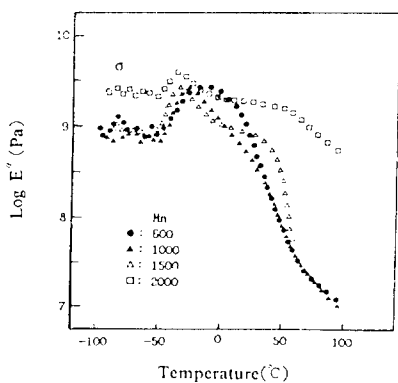


Figure 3. (b)

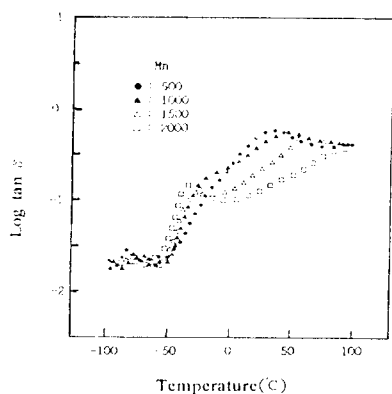


Figure 3. (c)

Figure 3. Dynamic mechanical properties of the emulsion cast films.

a) storage modulus(E'),
b) loss modulus(E''), and c) $\tan \delta$

4.5 Swelling in Water and DMF

With the increase of Mn of PTAd from 600 to 2000, swell in DMF (Table 2) increases over 5 times, whereas in water increases slightly. The overall hydrophilicity of PU slightly increases with soft segment content. It seems that DMF is preferentially dissolved in soft domain. At low Mn (≤ 1000), swelling is favored by amorphous nature of the soft segment, and retarded by the hard domains dissolved in soft segments. At high Mn, swelling is augmented by phase separation and retarded by the crystallinity of the soft domain. It seems that the former dominates.

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