

Segmented Polyurethane Ionomer에 있어서의 Prepolymer 분자량의 영향

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Effect of Prepolymer Molecular Weight in Segmented Polyurethane Ionomers

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요 약 : 환상 지방족 isocyanate인 isophorone diisocyanate(IPDI)와, poly(tetramethylene adipate) glycol(PTAd), dimethylol propionic acid(DMPA)로 부터 polyurethane(PU) ionomer를 제조. 이를 물에 분산시킴으로써 안정된 수성 PU를 제조하였으며, prepolymer의 분자량(2000~6000)이 유화특성 및 emulsion cast film의 열적, 기계적 성질에 미치는 영향을 검토하였다. Prepolymer의 분자량 증가와 더불어 유화입경 및 인장물성(탄성률 및 강도)은 급격한 감소후 완만한 증가를 보였으며, 점도 및 신율은 대체적으로 이와 상반되는 경향을 보였다. 또한 soft segment T_m 및 T_g 는 prepolymer 분자량이 증가함에 따라 증가하는 경향을 나타내었다.

Abstract : Segmented polyurethane(PU) ionomers were prepared from isophorone diisocyanate (IPDI), poly(tetramethylene adipate) glycol(PTAd), and dimethylol propionic acid(DMPA) as an anioic center. The effect of prepolymer molecular weight(2000~6000) on the emulsion properties, and thermal and mechanical properties of emulsion cast film was investigated. Particle size and tensile properties(modulus and strength) showed a rapid drop followed by a mild increase with increase of prepolymer molecular weight. Emulsion viscosity and elongation at break showed opposite tendency to the above. Melting temperature(T_m) and glass transition temperature(T_g) of the soft segment moved toward higher temperature with the increase of prepolymer molecular weight.

INTRODUCTION

Considerable efforts have been made to elucidate the diverse structure-property relationships

of segmented polyurethane(PU).¹ Properties of these materials basically depend on the phase morphologies which result from thermodynamically incompatible nature of the soft and hard segments.

Factors affecting the microphase separation include composition of soft/hard segment, type and molecular weight of soft segment, segment compatibility, and preparation method.²⁻⁴

In segmented PU ionomers, the molecular weight of the prepolymer plays an important role in determining the dispersion characteristics and physical properties as well. This paper describes such effects with regard to the structure-property relationship of PU ionomers.

EXPERIMENTAL

Materials

Poly(tetramethylene adipate) glycol (PTAd, $M_n = 1016$, Dongsung Chemicals) was dried at 80°C under 0.1 mmHg until no bubble was observed. Triethylamine (TEA) was used after treating over 3Å molecular sieve for 3 days. Other extra pure grades of dimethylol propionic acid (DMPA, Aldrich), triethylene tetramine (TETA, Junsei Chemical), N-methyl-2-pyrrolidone (NMP), and isophorone diisocyanate (IPDI, Huls AG) were used without further purifications. Extra pure grade of dibutyltin dilaurate (DBT, T-12) was employed as a catalyst.

Procedure

A 500 ml round-bottom, 4-necked separable flask with a mechanical stirrer, thermometer, condenser with drying tube, and a pipet outlet was used as the reactor. Reaction was carried out in a constant temperature oil bath. PTAd, DMPA, NMP, and DBT were charged into the dried flask. While stirring, the mixture was heated to 80°C for about 30 min, followed by adding IPDI to the homogenized mixtures. The mixture was heated to 80°C for about 3 hrs to obtain NCO-terminated prepolymers. The change of NCO value during the reaction was determined using a standard dibutylamine back titration method.⁵ Upon obtaining the theoretical NCO value, the prepolymers were cooled to 60°C, and triethylamine (TEA) was added and stirred for 1 hr while maintaining 60°C. The number average molecular weight of NCO-termi-

nated prepolymer with theoretical NCO value, which is determined by the formulation, will be referred to M_p .

While stirring rapidly, demineralized water was added to the solution to form water dispersion. TETA dissolved in water was then fed to the emulsion for a period of 40 min, and chain extension was carried out for the next 2 hrs. The resulting dispersion with a solid content about 30 wt% was stable over six months at room temperature.

Tests

Average particle size of the dispersion was measured using an Autosizer (Malvern II C) after treating the samples with ultrasonic waves. The viscosities of emulsion at 25°C were measured using Brookfield viscometer (DV-1, LV type). Thermal properties of the emulsion cast films were determined from differential scanning calorimetry (DSC, Du Pont 910), and mechanical properties were measured using an Instron tensile tester with a crosshead speed of 200 mm/min.

RESULTS AND DISCUSSION

Particle Size and Viscosity of Emulsion

Fig. 1 shows that particle size decreases rapidly with M_p up to 4000, and further increase of M_p gives a mild increase in particle size. Essentially identical trend was observed in other systems.

Particle size of PU emulsion is primarily governed by the hydrophilicity of PU, i. e., particle size decreases with increasing hydrophilicity.^{6,7} In PU ionomer of the present system, the hydrophilicity is mainly controlled by the ionic content,^{7,8} which was fixed at 3.5wt% on total solid. As the M_p increases, the amount of isocyanate incorporated is reduced, resulting in substantial reduction of hydrophilic urethane linkage.

The finer particle obtained at higher M_p should be related to the viscosity of prepolymer solution. With the increase of M_p , the solution viscosity should increase. Emulsification was done by adding water to the prepolymer solution with rapid agitation, and eventually phase inversion and

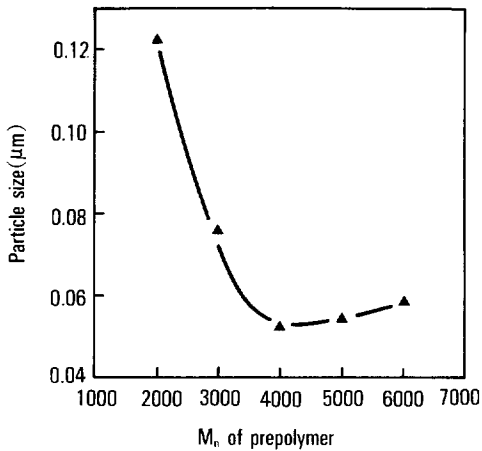


Fig. 1. Average particle size of PU ionomer as a function of M_p .

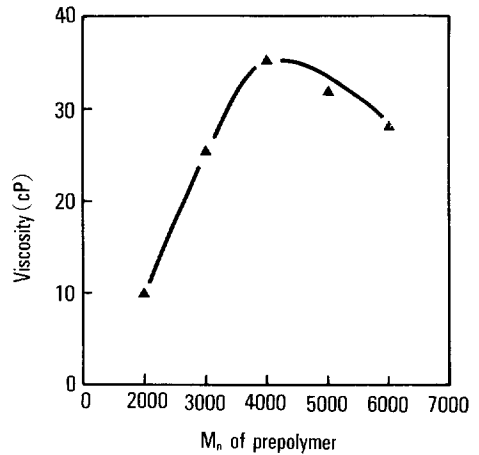


Fig. 2. Emulsion viscosity of PU ionomer as a function of M_p .

breakup of the organic phase occurred. At the stage of breakup, the viscosity of dispersed phase, or more precisely the viscosity ratio of the two phases should take a critical role in determining the particle size. It was observed that finer breakup was obtained when the viscosity of organic phase was significantly higher than water. Apparently, this makes a contradiction to what we believe in continuum mechanic, i. e., upon assuming the stress continuity. At the interface, shear stress is assumed continuous and hence finer breakup is obtained with smaller dispersed phase viscosity.⁹ The results shown in Fig. 1 may need further investigations.

Fig. 2 shows the viscosity of emulsions (solid content = 30wt%) as a function of M_p . Emulsion viscosity is governed by a number of factors such as concentration, size, and size distribution of particles,¹⁰⁻¹² and it is of practical significance in processing and various application areas.¹³ A number of theoretical and empirical approaches have become available and these are reviewed by Rutgers,¹⁰ and Saunders.¹⁴ Generally, larger particles with broad size distribution give lower emulsion viscosity at the same solid content. Our results indicate that viscosity increases over 3 times when the M_p increases from 2000 to 4000, beyond which it decreases

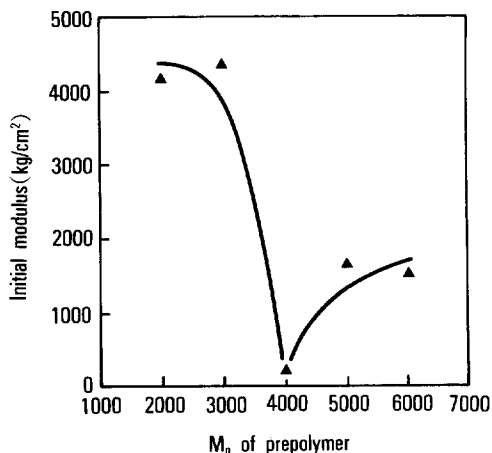
a bit. It seems that viscosity variation is governed by the variation of particle size (Fig. 1). In ionomer emulsion, particles are stabilized by the formation of electrical double layers,^{6,7} formed by anionic centers which are preferentially located at the surface of particles surrounded by the counter ions. These layers augment the interparticle attraction via Coulombic force and hydrodynamic volume under motion. This phenomenon known as electroviscous effect, causes increase of viscosity and this effect should be greater for smaller particles.

Thermal Properties

The results from DSC measurement are given in Table 1, where melting peak was observed only for $M_p \geq 4000$ (with slight increase with M_p), and T_g monotonically increased with M_p . With the increase of M_p , more of polyols and less of isocyanate is incorporated in PU structure, with substantial reduction in hard fraction and crosslinking as well. Ester type polyols form hydrogen bonds between the NH of urethane and the carbonyl of polyester segments,¹⁵ and hence higher degree of phase mixing is obtained with PU from PTAd. In addition, crosslinkings also prevent phase separation into soft and hard segments. Crystallization is possible only with certain level of phase separation^{16,17}

Table 1. T_g and T_m of Emulsion Cast Films

M_p	T_g (°C)	T_m (°C)
2000		
3000	-42.6	
4000	-39.4	42.0
5000	-32.1	43.8
6000		44.4

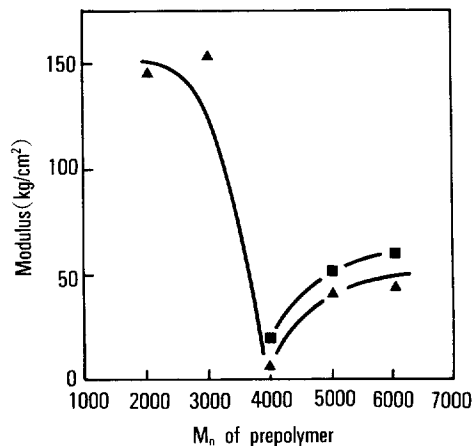
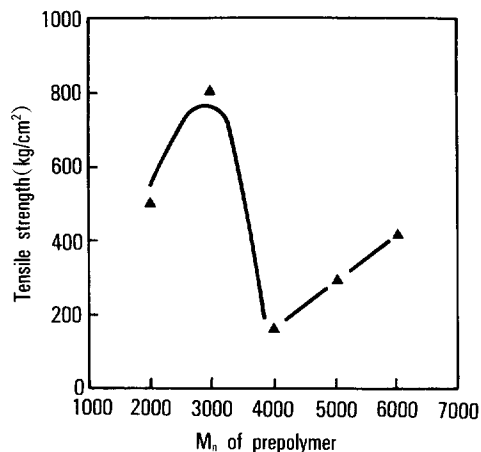
**Fig. 3.** Initial modulus of PU ionomer as a function of M_p .

which is favored with higher M_p from two aspects, i. e., increased soft segment fraction and reduced crosslinkings. Therefore, the T_m appeared for $M_p \geq 4000$ seems reasonable. Though marginal, the monotonic increase of T_m with M_p implies higher domain purity with the increase of M_p .

The increase of T_g of soft segment with the increase of M_p makes an apparent contradiction with the crystalline behavior. However, with soft segment crystallization at higher M_p , the concentration of hard segments in amorphous mixed domains should become greater, and this provides soft segment with rigidity and higher T_g .¹⁵

Mechanical Properties

Figs. 3 and 4 show a drastic drop of modulus at $M_p = 4000$, followed by a mild rise. In general, modulus reflects the rigidity of materials, and this property in PU is attributed to the hard segment

**Fig. 4.** Modulus of PU ionomer as a function of M_p (100% : \blacktriangle , 300% : \blacksquare).**Fig. 5.** Tensile strength of PU ionomer as a function of M_p .

fraction, crystallinity and crosslink density. With the increase of M_p , hard segment as well as crosslinking is reduced yet with on crystallinity. With further increase of M_p , the soft segments start to crystallize in such a way that modulus reduction due to the decreased hard fraction and crosslinking is overcome to some extent. This M_p may correspond to 4000 for the present system. As the M_p increase, the orientation of crystalline phase under strain due to phase separation seems more feasible, and strain hardening is observed (com-

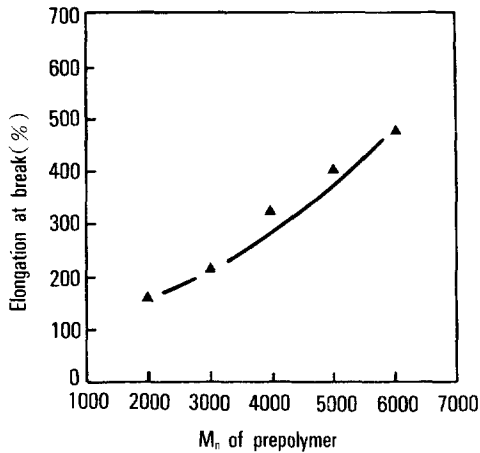


Fig. 6. Elongation at break of PU ionomer as a function of M_p .

pare modulus of 100% with that of 300%.

Tensile strength(Fig. 5) shows essentially identical trend with modulus. A sharp drop at $M_p=4000$ may be related to the phase separation of amorphous soft-hard segments, in addition to the reduction in hard fraction and crosslinking.¹⁵ Crystallization observed for $M_p \geq 4000$ should be responsible for increased strength. Elongation at break generally increases with M_p , due to the increase of soft segment and reduced crosslinking.

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