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김 상 준 · 이 영 민 · 김 병 규
부산대학교 고분자공학과
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Polyurethane Ionomers with Shape Memory Effect

Sang June Kim, Young Min Lee, and Byung Kyu Kim

Dept. of Polymer Science and Engineering, Pusan National University, Pusan 609-749, Korea
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요 약 : Hexamethylene diisocyanate(HDI), ether 및 ester형 polyol과 ionic center로서 trimellitic anhydride(TMA)를 사용하여 polyurethane(PU) 분산액을 제조하였으며, polyol의 종류 및 분자량 그리고 ionic center의 함량이 유화입자 및 점도에 미치는 영향과 아울러 용매증발법으로 제조한 film의 기계적, 점탄성적 성질에 미치는 영향을 검토하였다. 또한 본 실험에서 제조한 ionomer가 형상기억능이 있음을 감안, 이에 관한 기본적인 성질을 측정하였다.

Abstract : Polyurethane(PU) dispersions were prepared from hexamethylene diisocyanate(HDI), ether and ester type polyols, and trimellitic anhydride(TMA) as a potential ionic center. The effects of the type of polyol, molecular weight of polyol, and concentration of ionic center on the particle size and viscosity of emulsion, together with the mechanical and viscoelastic properties of the emulsion cast film were determined. In addition, basic properties concerning the shape memory effect of the ionomers were examined.

INTRODUCTION

Aqueous polyurethane(PU) dispersions offer the significant advantage of imparting the high performance properties of PU to a myriad of application area while eliminating the emission of organic solvent into the atmosphere.[1~5] Aqueous PU can be prepared in the form of ionic and nonionic type, and a number of ionic and potential ionic compounds are now available in the open literature.[6] On the other hand, aqueous PU can be prepared in acetone process, prepolymer mixing process, melt dispersion, Ketimine process etc..[6] Among them, acetone process is a most well established one, and uses acetone as an intermediate aid to control the viscosity during the critical chain extension step. Further, this process allows the use of aromatic as well as aliphatic type diisocyanate, and therefore structure-property architecture is more feasible.

This paper considers the preparation of PU ionomer dispersion ᵏfrom trimellitic anhydride (TMA) as a potential ionic center, hexamethylene diisocyanate(HDI), and polyol. Several types of polyols, i. e., polycaprolactone diol(PCL), polytet-

ramethylene adipate glycol(PTAd), and polytetramethylene glycol(PTMG) were used to compare the soft segment contribution. Effects of polyol molecular weight and contents of ionic centers, in terms of interionic molecular weight(Mi) were also examined. Particle size and viscosity of emulsion, and physical properties(thermal, viscoelastic, and mechanical) of the emulsion cast film were measured. In addition, the PU ionomer prepared in the experiments showed remarkable shape memory effect, and basic properties pertinent to the effect were also examined.

EXPERIMENTAL

PCL(Mn=850, 1500, 2000, Daicel), PTAd(Mn = 1000, Dongsung Chemicals) and PTMG(Mn = 1000, Dongsung Chemicals) were dried and degassed at 80℃, 0.1mmHg for 3 hrs.

Acetone and triethylamine(TEA) were treated with 3 Å molecular sieve overnight. Extra pure grades of other reagents, trimellitic anhydride (TMA), dibutyltin dilaurate(T-12), and hexamethylene diisocyanate(HDI) were used without further purifications.

Reactions were conducted in a 500ml four-necked round-bottom, flask with a mechanical stirrer, nitrogen inlet, condenser and pipette outlet. Excess amount of polyol and TMA(3.5 : 1 by mole) was charged to the flask, and heated to 100℃ for 1 hr to obtain monoester. The mixture was further heated to 190℃ for the next approximately 4 hrs to obtain diesters, which were subsequently dried in vacuum at 60℃ for 3 hrs. Formation of monoester and diester was followed by measuring the acid values.

Appropriate amounts of polyols were mixed with the prepolymers, and neutralized with TEA for 20 min at 50℃. HDI, dissolved in acetone, was subsequently added to the mixture. In about 3 hrs of reaction, the infrared absorpsion peak of the mixture at 2270 cm^{-1}, corresponding to NCO streching,[7] has completely disappeared.

Aqueous dispersion of PU was obtained by ad-ding water to the mixture at 60℃ and 500 rpm. A tubing pump was used to control the water addition. Upon completing emulsification, acetone was distilled off at 40℃ and 400 mmHg, and the solid content in final product was around 30%.

Particle size and its distribution were determined from Autosizer(Malvern IIC) after ultrasonic treatments. The viscosities of emulsion at 25℃ were measured using a cone-and-plate type viscometer(Tokyo Keiki ELD 1942).

PU films were cast from emulsion on a Teflon plate and dried at 40℃ for 12 hrs. The remaining moisture was removed at 30℃, 20mmHg for the next 24 hrs.

Thermal properties of the films were determined from differential scanning calorimetry(DSC, du Pont 910), and the mechanical properties from an Instron following the procedures described in JIS 6301 with a crosshead speed, 100 mm/min. For DSC measurements, samples were first quenched to -95℃ with liquid N$_2$, and were heated to 80℃ at 10℃/min. Melting peak temperature(Tm) was measured during the second heating cycle from 0 ℃ to 80℃, at 10℃/min. Viscoelastic properties of the film were determined from Rheovibron(Toyo Baldwin DDV-Ⅱ). Measurements were made from -115 to 80℃ at 11 Hz.

RESULTS AND DISCUSSION

Particle Size and Viscosity of Emulsion

Average particle size of emulsion as a function of interionic molecular weight(Mi) is shown in Fig. 1. Regardless of the type of polyol used, particle size increases with the increase of Mi. This is primarily due to the decreased hydrophilicity of PU with increasing Mi.[6] The ionic group is hydrophilic in nature, and hence more incorporations of ionic centers in PU structure will augment the amount of total hydrophilicity, and reduction in particle size results.[8] Since Mi is defined as the molecular weight of PU segment between the ionic centers, increase in Mi dictates reduced fraction of ionic center and hydrophilicity, and the results are
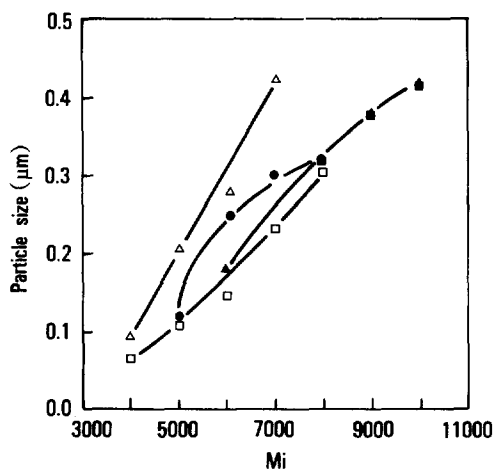
Fig. 1. Average particle size vs. Mi of PU emulsions : ● (PCL, 850), ▲ (PCL, 1500), ■ (PCL, 2000), △ (PTAd, 1000), □ (PTMG, 1000).

Fig. 2. Emulsion viscosity vs. Mi at 25℃(solid content, 30%) : ● (PCL, 850), ▲ (PCL, 1500), ■ (PCL, 2000), △ (PTAd, 1000), □ (PTMG, 1000).

as expected.

With regard to the effect of polyol, average particle size of PU emulsion is in the increasing order of PTMG < PCL < PTAd, an order consistent with the decreasing solubility parameter of polyols incorporated, i. e., 8.90(PTMG), 8.63(PCL), and 8.53 (PTAd). It may be seen that the particle size slightly decreases with the increase of polyol molecular weight(PCL), however the effect is marginal.

Fig. 2 shows the viscosity of the emulsion(solid content, 30 wt%) as a function of Mi, where viscosity decreases with the increase of Mi. The viscosity of emulsion, prepared from different types of polyol, is in the increasing order of PTAd < PCL < PTMG, an order exactly the opposite to the average particle size. It is also noted that the viscosity changes over two order of magnitude, depending on the Mi, for PU from PTMG.

The decrease of viscosity with increasing Mi is directly relatable to the increase of particle size with Mi.[9] PU ionomer in aqueous media is stabilized by the formation of electrical double layers.[10] That is, at the ionomer-water interface, a double layer is formed by the dissolution of salt groups, which in effect is to increase the hydrodynamic volume of the particle when in motion, and exerts more resistance to flow. At fixed solid content,
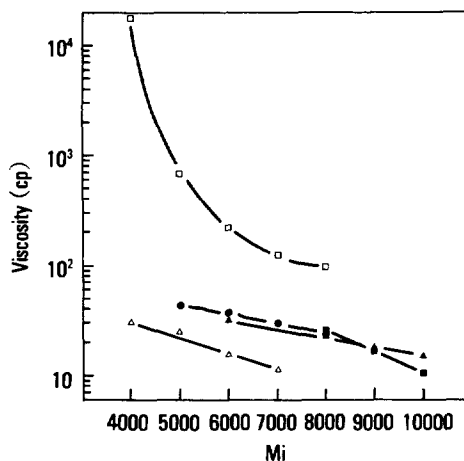
smaller particle will lead to larger hydrodynamic volume, and consequently the emulsion viscosity will increase. The difference in emulsion viscosity for the three types of polyol, would also be explained from the difference in particle size, i. e., smaller particle gives higher viscosity at the same solid content.

Thermal Properties

Typical thermal properties of the ionomers are shown in Figs. 3 and 4 for PU prepared from PCL. The melting peak temperature(Tm) of soft segment is almost independent of Mi(Fig. 3), but increases over 13℃ when the Mn of PCL increases from 850 to 2000(Fig. 4). Significant increase of Tm with Mn of PCL is probably due to the hard-soft phase separation at high molecular weight of polyol,[11] the phenomenon generally is made use of for PU architecture. With clean phase separation, packing of soft segments into crystalline structure is more feasible. This should lead to the increase in crystallinity as our result(Fig. 4) indicated.

Total heat of fusion(ΔH_f) also increases with Mi(Fig. 3). With the increase of Mi, more of polyol will be incorporated in the PU structure. In addition, intermolecular interactions will be reduced due to the reduced Coulombic forces between the ionic centers, and reduced hydrogen bondings
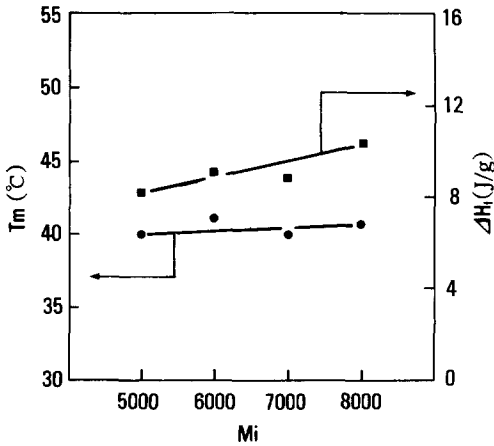
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Fig. 3. Tm and ΔH_f vs. Mi(PCL, Mn=850).

Fig. 4. Tm and ΔH_f vs. Mn(PCL, Mi=8000).

Fig. 5. Storage modulus vs. temperature of PU from PCL with different value of Mi : $\triangle$(5000), $\blacktriangle$(6000), $\bigcirc$(7000), $\bullet$(8000).

Fig. 6. Loss modulus vs. temperature of PU from PCL with different value of Mi : $\triangle$(5000), $\blacktriangle$(6000), $\bigcirc$ (7000), $\bullet$(8000).

predominantly between ionic centers and urethane linkages.[12] Since, the ionic center(TMA) is located between two soft segments(PCL) in the present system, reduction in ionic centers will also contribute to the soft-hard phase separation. With larger phase separation, more of soft segment crystallization is expected, as our results indicate.

Viscoelastic Properties

The elastic moduli of the ionomers with different Mi are shown in Figs. 5 and 6 for PU from PCL. The major relaxation shown should correspond to the glass transition of soft segment. It is seen that the relaxation becomes sharp as Mi inc-
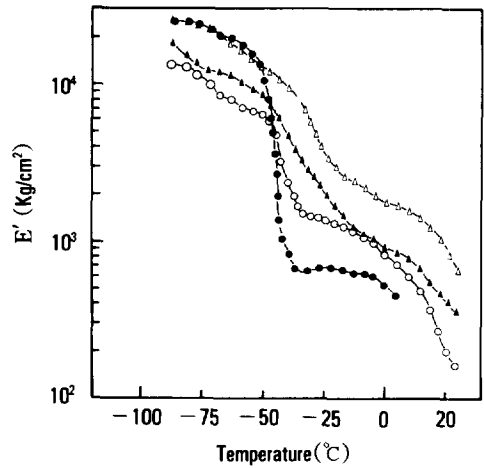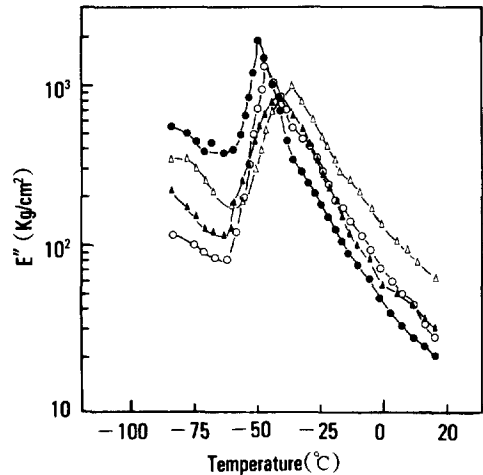
reases due probably to the reduced interactions between the soft and hard segments leading to easier domain separation. In addition, at 8000 Mi relatively well defined rubbery plateau exists, and the value reads approximately $6 \times 10^2 (Kg/cm^2)$. The existence of the plateau indicates extensive entanglements of the chains which, in general, reflects molecular weight effect. However, simple cal-

Table 1. Formulations of the Feed for PUs from PCL $(M_n = 850)(g)$

Mi^1	DPM^2	Polyol	HDI	TEA(ml)	Mn of PU
5000	25.192	9.56	5.35	2.78	66715
	(0.0200)	(0.0113)	(0.0319)		
6000	20.99	13.53	5.58	2.32	66473
	(0.0167)	(0.0159)	(0.0332)		
7000	17.99	16.37	5.75	1.99	66938
	(0.0143)	(0.0193)	(0.0342)		
8000	15.75	18.50	5.87	1.74	66703
	(0.0125)	(0.0218)	(0.0349)		

catalyst : dibutyltin dilaulate(0.1wt%), acetone : 75g, water : 93.3g

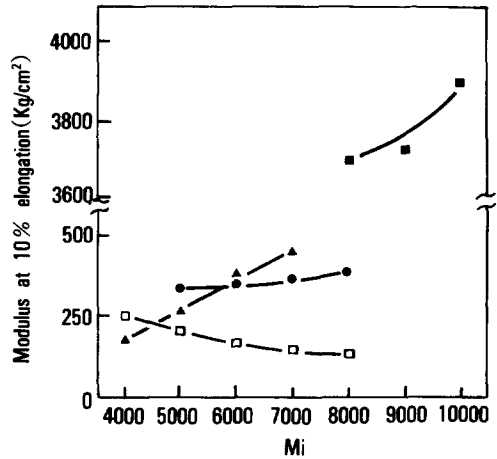[a] $Mi = 1.25[M_{diester\ mix.} + PCL + M_{HDI}(PCL/M_{PCL} + 1)]$

[b] diester prepolymer mixture (　　) : mole

Fig. 7. Modulus vs. Mi of PUs from various polyol : ●(PCL, 850), ■(PCL, 2000), ▲(PTAd, 1000), □ (PTMG, 1000).

culation using the formula given in Table 1 indicates that the number-average molecular weight (Mn) of PU is almost independent of Mi. Therefore, the existence of rubbery plateau at the highest Mi should represent the morphology of the PU. It is convincing that hard domains act as the tie points in plateau region. When the hard domain fraction is small(presently less than 14%), it is expected that phase separated hard domains would work effectively as tie points than homogeneously distributed ones.

As Mi increases, the glass transition temperature moves toward the lower temperature. It may be worth to mention that the T_g decreased by approximately 5℃ at 8000 Mi as the Mn of PCL increased from 850 to 2000(not shown).

Mechanical Properties

The tensile modulus(10% elongation) of the emulsion cast film, determined using an Instron, is shown in Fig. 7. The modulus increases, except PTMG, with the increase of Mi, a contradiction to the Rheovibron data. The contradiction may not be properly explained without resorting to the different strain levels tested. Rheovibron measurements correspond to linear viscoelastic property, whereas measurements were made at 2% strain. At such low strain, PU responds as a whole and the properties obtained should close to the bulk

properties.[13] As the strain increases, soft domain first deforms, followed by the orientation of hard domain as a whole. As the elongation further increases, hard domain deforms, and the level of strain where the hard domain deformation starts should depends on the phase morphology and interchain interactions.[14,15]

The tensile modulus measured at 10% strain should represent the soft domain characteristics. As was shown from the DSC data (ΔH_f), crystallinity increased with the increase of Mi, and an increase in modulus should results.

With regard to the type of polyol, PCL and PTAd gave higher modulus compared to that of PTMG at the same value of Mi. This should be the polyol characteristics. In general, ester type gives higher mechanical properties over the ether type due to the better interchain interactions.[14]

The ultimate tensile strengths of the emulsion cast films are shown in Fig. 8. The effect of the type of polyol on tensile strength is qualitatively the same with the effect on tensile modulus. However, tensile strength decreases with increasing Mi, an apparent contradiction to the modulus dependence. Tensile strength corresponds to the highest strain that the materials can sustain. At this
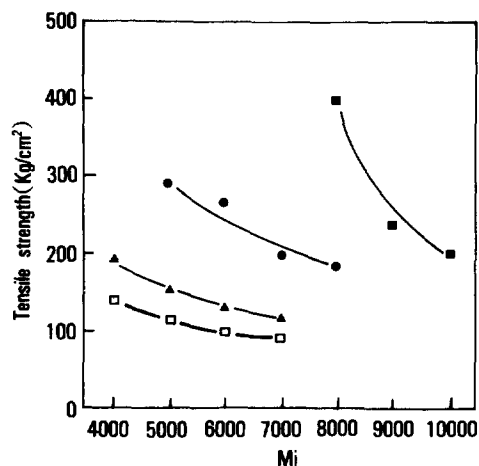
Fig. 8. Tensile strength vs. Mi of PUs from various polyol : ●(PCL, 850), ■(PCL, 2000), ▲(PTAd, 1000), □(PTMG, 1000).
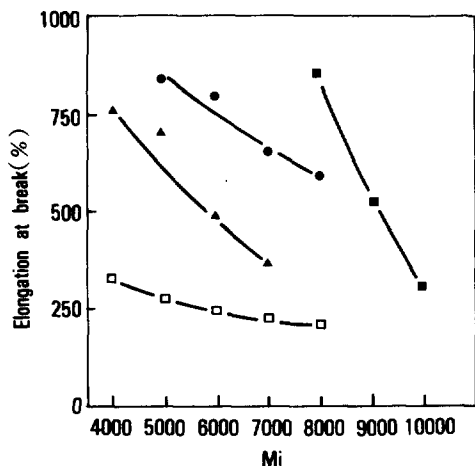

Fig. 9. Elongation at break vs. Mi of PUs from various polyol : ●(PCL, 850), ■(PCL, 2000), ▲(PTAd, 1000), □(PTMG, 1000).

Table 2. Time Required for Perfect Return to Original Shape at Various Temperatures(min : sec)

Polyol	Mi	Tm	40°C	45°C	50°C	55°C	60°C
PCL	5000	40°C	4 : 30	2 : 30	1 : 20		
850	6000		3 : 00	2 : 00	0 : 58		
	7000		1 : 40	1 : 20	0 : 40		
	8000		2 : 00	0 : 45	0 : 45		
PCL	8000	53°C			3 : 10	0 : 50	
2000							
PTAd	5000	43°C		4 : 00	3 : 00	0 : 55	
1000	6000			2 : 50	1 : 30	0 : 40	
	7000			2 : 50	0 : 50		

nsile properties at high elongation. With reduced interchain interactions accompanied by phase separation along the increase of Mi, reduced tensile strength(Fig. 8) and elongation at break(Fig. 9) could be expected.

Shape Memory Effect

Polymers with excellent shape memory effect have recently been discovered, and a number of potential applications inculding autocholk valve, fire alarm, pipe joint, etc. are considered.[16,17] Commerciallized item includes trans-polyisoprene, styrene-co-butadiene, and polyurethane resins. Such polymers are, in principle, built of two phases, i. e., fixed points imbedded in reversible phase. In the present experiments, specimen($1.0 \times 10 \times 0.03$ cm) was instantaneously elongated to 300% at room temperature, and the shape memory effect was observed in a constant temperature chamber (± 0.5°C). It is seen from Table 2 that the shape memory starts at temperature corresponding to the Tm of polyol. As temperature increases, the memory effect becomes faster, in a similar fashion to entropy elasticity. As Mi increases, shape recovery responds more quickly. This probably is a charateristic, pertinent to ionomer. In PU ionomer, the elongation set increases with increasing ionic center,[18] due presumably to the formation of new physical crosslinking or ionic bondings.

level of strain, hard domain as well as soft domain is fully deformed. Therefore fraction of hard domain, interchain interactions, and the degree of phase separation all together contribute to the ultimate properties. However, hard domain fraction is insignificant, and hence interchain interactions and phase separation should mainly govern the te-

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