

Polyurethane Ionomer의 상분리구조의 동적해석

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Dynamic Analysis of Microphase Separations in Polyurethane Ionomers

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요약 : PMVL, PCL, PTAd 및 IPDI로부터 prepolymer 혼합법에 따라 음이온형 수성 폴리우레탄(PU)을 얻었다. 이때 구조변수로서는 이온 및 BD함량, 연결상의 형태 및 길이로 하였으며 emulsion 주조 필름을 이용, PU 조성 및 구조변화에 따른 연결상-경질상간의 상분리를 연구하였다. 상분리는 연결상 길이에 매우 민감하였다. 상분리시에만 고무상 탄성율의 값이 매우 컸으며, 상분리는 PCL이나 PMVL 보다 PTAd로 된 PU가 훨씬 뚜렷하였다.

Abstract : Waterborne polyurethanes (PU) anionomers were obtained from poly(β -methyl- δ -valerolactone) glycol (PMVL), poly(caprolactone) glycol (PCL), poly(tetramethylene adipate) glycol (PTAd), and isophorone diisocyanate (IPDI) following a prepolymer mixing process. The soft-hard segment phase separations in response to the variations of composition and structure of PU have been studied from the dynamic mechanical measurements of the emulsion cast film. The structural variation included ionic and butanediol (BD) content, and type and length of the soft segment. It was found that phase separation was sensitive to the soft segment length. With only phase separation, the rubbery modulus was significant even with lower hard segment content. Phase separation was much greater with PU from PTAd, rather than the one from PCL and PMVL.

Keywords : polyurethane ionomer, PMVL, IPDI.

INTRODUCTION

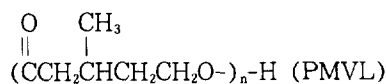
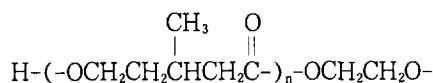
Polyurethanes (PU) aqueous dispersions are nontoxic, nonflammable, and do not pollute the air. They can be prepared in the form of ionomer and nonionomer as well. Nonionomer type should contain hydrophilic soft segment such as polyethylene glycol, whereas the ionomer type contains pendant acid or tertiary ni-

trogen groups which are neutrallized to form salts. The properties of PU ionomers are primarily governed by the phase behavior of soft and hard segments as well as ion character.

The existence of the hard segment domains 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 dis-

solved hard segment.^{3,4} In general, the polyester soft segment was found to contribute phase mixing by hydrogen bonding between the soft segment and hard segment.^{5,6} This behavior also depends on the content, length, and polarity of soft and hard segments. A large number of previous investigations⁷⁻¹¹ have reported on the characterization of this microdomain structure in segmented PU. However, little has been evolved regarding the ionomer type PU dispersions since most work in this area has been done by industrial laboratories, and basic structure/property behavior is sparse in the open literature.¹²⁻¹⁴

This paper considers preparation and dynamic mechanical properties of ionomer type waterborne PU from an aliphatic diisocyanate viz., isophorone diisocyanate (IPDI) and poly(β -methyl- δ -valerolactone) glycol (PMVL), poly(ϵ -caprolactone) glycol (PCL) and poly(tetramethylene adipate) glycol (PTAd), following a prepolymer mixing process. The effects of ionic and butanediol (BD) content, and type and length of the soft segment are considered in terms of dynamic mechanical properties of the emulsion cast films, with an emphasis on the microphase behavior. The advantage of using PMVL lies in its hydrolytic stability, and prohibition of soft segment crystallization due to the pendant methyl group (see the structure below).



EXPERIMENTAL

Materials. PMVL (Daicel), PCL (Daicel), and

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

Prepolymer Synthesis. Basic formulations are given in Table 1. A 500 mL 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

Table 1. Feed Compositions of Polyurethane Ionomers (unit : g)

A. Effect of DMPA Content

RUN#	PMVL1000	IPDI	DMPA (wt %)	TEA (mL)	TETA
A-1	31.49	11.37	1.12(2.5)	1.17	0.706
A-2	30.87	11.61	1.35(3.0)	1.40	0.703
A-3	30.25	11.85	1.57(3.5)	1.64	0.701
A-4	29.63	12.09	1.80(4.0)	1.87	0.698

B. Effect of BD Content

RUN#	PMVL2000	IPDI	DMPA (wt %)	BD (wt %)	TEA (mL)	TETA
B-1	33.21	8.75	1.57(3.5)	0.00(0)	1.64	0.70
B-2	31.80	9.75	1.57(3.5)	0.45(1)	1.64	0.70
B-3	30.39	10.76	1.57(3.5)	0.90(2)	1.64	0.70
B-4	28.99	11.76	1.57(3.5)	1.35(3)	1.64	0.70
B-5	27.58	12.76	1.57(3.5)	1.80(4)	1.64	0.70

C. Effect of Soft Segment Type

RUN#	POLYOL	IPDI	DMPA (wt %)	TEA (mL)	TETA
C-1	PMVL (33.21)	8.75	1.57(3.5)	1.64	0.70
C-2	PMVL (33.12)	8.83	1.57(3.5)	1.64	0.70
C-3	PCL (33.21)	8.83	1.57(3.5)	1.64	0.70

temperature oil bath. PMVL, BD, DBT(0.03 wt% based on the total feed), and DMPA dissolved in DMF(5 wt% based on the total charge) 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 3hr 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 feed) was added and stirred for 1hr while maintaining the temperature at 60 °C. The 1:1 stoichiometry was obtained by adding TETA at chain extension step.

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

Tests. Dynamic mechanical tests were performed with a Rheovibron (Orientec, DDV-01FP) from -100 °C to 100 °C at a frequency of 11 Hz, with a sample size of 0.03 × 0.2 × 3 cm. Films were prepared by casting the emulsion on a teflon plate, followed by drying at 80 °C for 5hr. The resulting films were then heated overnight in an oven at 60 °C under 2

~3 mmHg. The crystalline structures were examined with an X-ray diffractometer (Rigaku model D/MAX-2400) using Cu-K α radiation from 2~40° at a scan speed of 4°/m(30kV, 16mA).

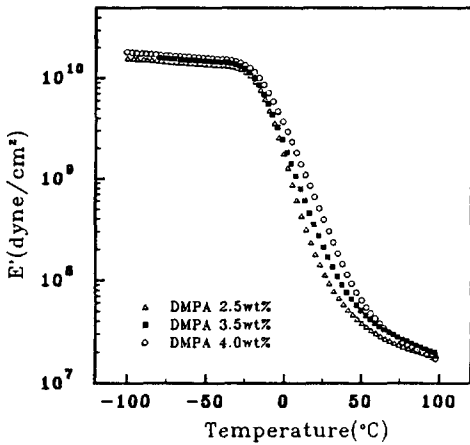
RESULTS AND DISCUSSION

Effect of Ionic Content. This series of experiments used PMVL1000(number designates number average molecular weight) at a fixed prepolymer molecular weight(M_{pre}=4500). The concentration of DMPA varied 2.5~4.0 wt% based on total solid.

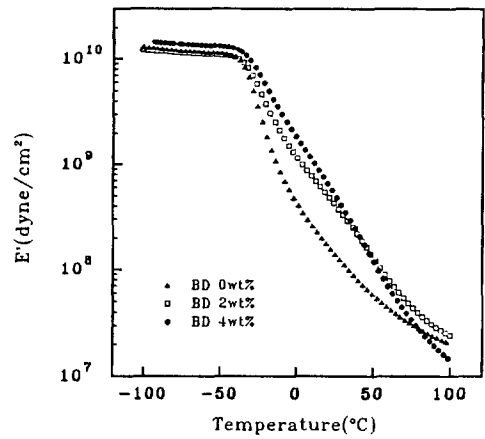
Fig. 1 shows the dynamic mechanical properties of the emulsion cast films. Storage modulus(E') (Fig. 1a) generally increases, and the major transition temperature (Fig. 1b) moves toward the higher temperature as the DMPA concentration increases. It seems that the soft and hard segments of these PUs are virtually phase mixed morphology to show a single glass transition(T_g). The microphase miscibility is likely due to the relatively short soft segment, coupled with the strong hydrogen bondings between oxygens of the lactone groups, especially the carbonyl group oxygens, and the hydrogen atoms of urethane groups.¹¹ The increase of storage modulus and T_g with DMPA concentration is mainly driven by the increased hard content(isocyanate+DMPA+TEA+TETA) and Coulombic forces between ionic centers.

With regard to the mechanical properties, hardness, modulus, and tensile strength increase, and elongation at break decrease with DMPA concentration (Table 2A series). In segmented PU, soft segments contribute to the elasticity and low temperature properties, whereas the hard segments to the modulus, strength and elevated temperature properties, and the results in the Table 2 are expected.

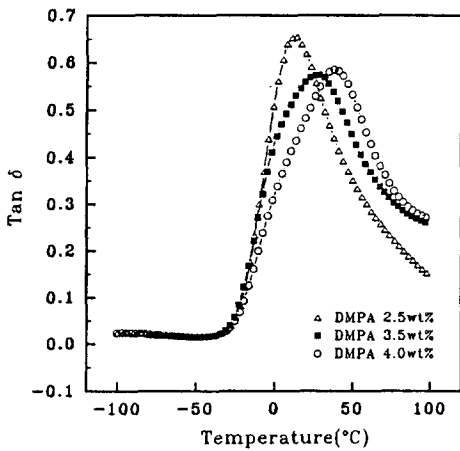
Effect of Butanediol Content. This experiments were done at a fixed DMPA con-



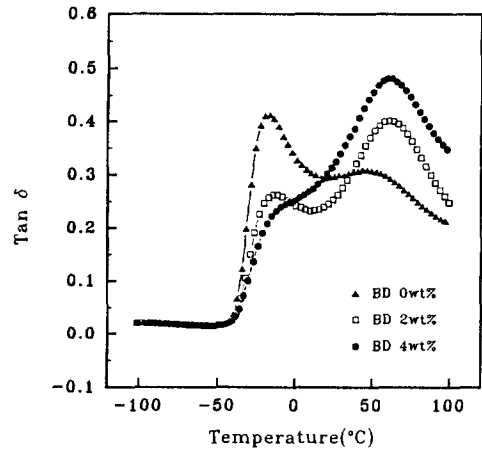
(a)



(a)



(b)



(b)

Fig. 1. Dynamic mechanical properties of emulsion cast films as a function of DMPA content : (a) storage modulus(E') and (b) $\tan\delta$.

Fig. 2. Dynamic mechanical properties of emulsion cast films as a function of BD content : (a) storage modulus(E') and (b) $\tan\delta$.

centration(3.5 wt%) and M_{pre} (4500) using P-MVL2000. The content of BD varied 0 ~ 4 wt% based on total solid, corresponding to a hard segment content of PU, 25~38 wt%.

Fig. 2 shows that dynamic mechanical properties of the ionomers. With increasing BD, glass state and room temperature storage moduli increase. However, the tendency is reversed while nearing the rubbery region,

where PU containing 4 wt% BD(the highest content) shows the lowest modulus. The effect of BD on elastic modulus should be closely related to the microphase morphology of the PU. The $\tan\delta$ peaks(Fig. 2b) of the ionomers give a clue to the soft segment hard segment phase morphology.¹⁸ The $\tan\delta$ curve of 2 wt% BD designates two well defined peaks, each corresponding to the T_g of soft

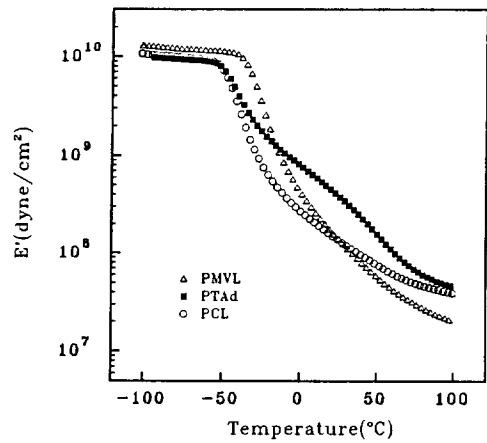
segment(T_{gs}) and hard segment(T_{gh}). With 0 wt% BD, the T_{gs} is a well defined peak, but T_{gh} is a broad one. On the contrary, with 4 wt% BD, T_{gs} is a mere shoulder, whereas T_{gh} is a large and well defined. Based on T_g behavior, the PU ionomers in this series are phase separated(0, and 2 wt% BD), or partial miscible(4 wt% BD), and the soft-hard phase separation is mainly driven by the high molecular weight of PMVL2000. It is further noted that both T_{gs} and T_{gh} move toward the higher temperature with increasing BD content, due probably to the dissolved hard segments in soft segments domains by increased phase mixing(higher T_{gs}) and increased cohesion of hard segments(higher T_{gh}). The lowest rubbery modulus with 4 wt% BD is presumably due to the greater soft segment and hard segment phase mixing of this PU.¹⁸ Reinforcing effect by hard segments in rubbery state is expected with only certain extent of phase separation viz., the size of imbedded domain, rather than the amount. On the other hand, in glass state, the composition governs the modulus.

Hardness, modulus, and tensile strength, measured at room temperature, increase and elongation at break decreases with the content of BD(Table 2B series). This is primarily driven by the increased hard fraction(25→38 wt%), but more or less retarded by the partial phase mixing with 4 wt% BD.

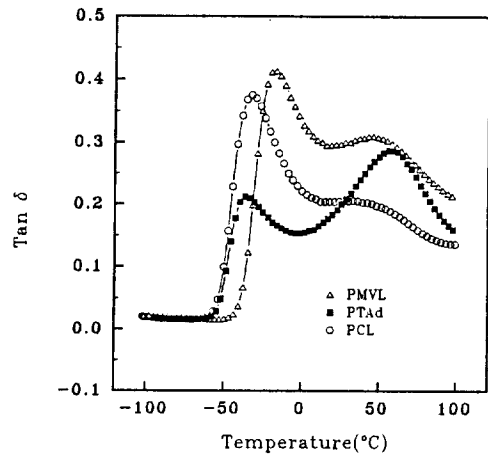
Effect of Soft Segment Type. This experiments were formulated with PTAd, PCL, and PMVL with same molecular weight(2000), and at a 3.5 wt% DMPA, and $M_{pre}=4500$.

Fig. 3 shows the dynamic mechanical properties of the three types of PUs. PMVL PU shows the highest glass modulus and lowest rubbery modulus, whereas PTAd PU shows the lowest glassy modulus and highest rubbery modulus. This may be related to the extent of soft segment-hard segment phase separation. The $\tan \delta$ curves show two well de-

finer peaks for PTAd PU, but a well defined soft segment T_g , and broad one for PMVL PU, and a mere shoulder for PCL PU for hard segments. Also, PTAd PU shows two T_{gs} of the lowest soft segment and highest hard segment in the three types of PUs. Based on this, phase separation is most pronounced with PTAd PU. The greatest phase separation for PTAd PU was, at a



(a)

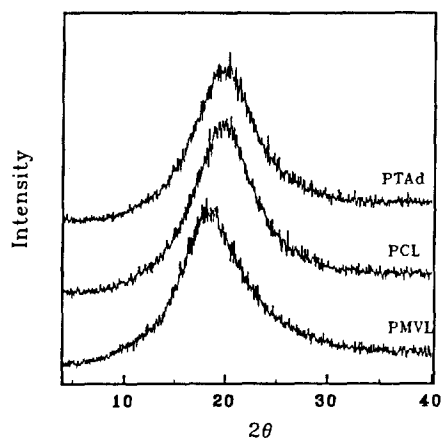


(b)

Fig. 3. Dynamic mechanical properties of emulsion cast films as a function of soft segment type : (a) storage modulus(E') and (b) $\tan \delta$.

Table 2. Emulsion Characteristics and Physical Properties of Waterborne Polyurethanes

RUN	Particle Size(nm)	Viscosity (cPs)	Hardness	Modulus (kg/cm ²)		Tensile Strength (kg/cm ²)	Elongation at Break(%)
				Initial	300%		
A-1	298.9	6.3	55.0	215.5	35.5	315.5	597.0
A-2	130.0	7.0	58.5	283.1	37.6	336.4	528.0
A-3	91.0	7.3	61.0	502.2	43.8	390.5	498.9
A-4	84.0	7.5	68.0	784.3	78.5	455.6	455.6
B-1	71.1	7.5	57.8	114.0	21.0	261.7	693.0
B-2	80.0	7.2	65.0	163.8	24.3	287.0	644.1
B-3	87.7	6.9	72.8	405.2	33.0	303.2	583.3
B-4	115.6	6.7	76.0	623.0	48.7	327.0	549.6
B-5	143.0	6.3	80.5	624.9	55.1	345.4	540.0
C-1	71.1	7.5	57.8	114.1	21.8	261.7	693.0
C-2	81.6	11.5	76.8	382.9	44.8	472.2	516.7
C-3	83.7	10.5	64.0	145.7	21.3	324.0	546.0

**Fig. 4.** X-ray diffraction profile of emulsion cast films prepared from different type of soft segment.

time, presumed due to the crystallization of soft segment. However, DSC (differential scanning calorimetry) and X-ray diffraction (Fig. 4) shows no evidence of crystallization. In fact, the three types of PU films were all transparent. It seems that lactone groups of soft segment form stronger hydrogen bonding with urethane groups of hard segments than the ester groups of PTAd do.^{11,19} The methyl pendant groups of PMVL provide the soft

segments with rigidity, resulting in higher T_g of soft segment by over 15°C, as compared with PCL.

Hardness, modulus, and tensile strength at room temperature are significantly higher for PTAd PU. This is probably due to the stronger soft segment cohesion and greater soft segment-hard segments phase separation (Table 2C). Among lactone type soft segments, PCL PU is superior to the PMVL PU. The pendant methyl group of PMVL should disturb the close packing of soft segment, and reduces the soft segment cohesions leading to the inferior properties. The elongation at break is over 500% for three types of PUs. Such high ductility is due to the high soft segment content(78%) and phase separations.

CONCLUSIONS

The soft and hard segments of waterborne PUs prepared from PMVL1000 and IPDI formed virtually phase mixed morphology based on the single $\tan \delta$ peak, and the peak temperature(T_g) moved toward the higher temperature with increasing DMPA content. The increased T_g with DMPA was interpreted-

ed in terms of increased hard segment content and Coulombic forces between ionic centers.

Soft segment-hard segment phase separations were obtained with PMVL2000. Regarding the effect of BD in PMVL2000 experiments, phase separations were most pronounced with 2 wt% BD. It was concluded that the soft segment length rather than soft segment content is driving force for phase separations.

Soft segment-hard segment phase separations were most pronounced when PTAd, rather than PMVL or PCL, formed the soft segments. This implies that hydrogen bondings between oxygens of lactone groups and NH of urethane groups are greater than those of the oxygens of ester group with NH of urethane groups. On the other hand, the pendant methyl groups provided PMVL with stiffness, resulting in the higher soft segment T_g .

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