

## 환상 지방족 Isocyanate 및 Polytetramethylene Glycol로 제조한 수성 Polyurethane : 2. 쇠연장제 함량이 분산 및 Film 물성에 미치는 영향

이 영 민 · 김 병 규 · 신 영 조 · 조 현 흑\*  
부산대학교 고분자공학과 · \*부산대학교 섬유공학과  
(1992년 3월 27일 접수)

## Aqueous Polyurethanes from Cycloaliphatic Diisocyanate and Polytetramethylene Glycol : 2. Effect of Extender Content on Dispersion and Film Properties

Young Min Lee, Byung Kyu Kim, Young Jo Shin, and Hyun Hok Cho\*  
*Dept. of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea*  
*\*Dept. of Textile Eng., Pusan National University, Pusan 609-735, Korea*  
(Received March 27, 1992)

**요 약 :** 환상 지방족 isocyanate인 methylene bis(4-cyclohexyl isocyanate)(H<sub>12</sub>MDI) 및 isophoron diisocyanate(IPDI)와, polytetramethylene glycol(PTMG), 1,4-butanediol(BD, 쇠연장제) 및 dimethylol propionic acid(DMPA)로부터 polyurethane(PU) ionomer를 제조, 이를 물에 분산시킴으로써 안정된 수성 PU를 제조하였으며, 쇠연장제의 함량이 분산 입경 및 emulsion cast film의 물리적 성질에 미치는 영향을 검토하였다. BD의 함량이 증가할수록 유화입경, 인장 물성(탄성률 및 강도)은 증가하였고, α-완화는 고온으로 이동되었으며 무정영역의 상호인력 역시 증가함을 알수 있었다. 전반적으로 H<sub>12</sub>MDI계 PU가 IPDI계 PU에 비해 유화입경이 작고, 기계물성이 우수하게 나타났다.

**Abstract :** Segmented polyurethane(PU) ionomers were prepared from cycloaliphatic diisocyanate (methylene bis(4-cyclohexyl isocyanate) (H<sub>12</sub>MDI), isophoron diisocyanate(IPDI)) and polytetramethylene glycol(PTMG) using 1,4-butanediol(BD, chain extender) and anionic type chain extender, viz. dimethylol propionic acid(DMPA). The effect of BD on the state of dispersion and physical properties of emulsion cast film was determined using Autosizer, transmission electron microscopy(TEM), Instron, and Rheovibron. With more incorporation of BD in PU, particle size of emulsion, tensile modulus and strength of the emulsion cast film increased, and the major transition of soft segment moved toward higher temperature. With regard to the structural effect of the isocyanate, H<sub>12</sub>MDI gave finer dispersion, and better mechanical properties over IPDI.

## INTRODUCTION

Aqueous polyurethane(PU) is non-toxic, non-flammable, and does not pollute the air. Ideally, only water evaporates during the drying process. In addition, in aqueous PU dispersion chain extension between NCO-terminated prepolymers occurs in the form of dispersion. Consequently it is possible to set mole mass to practically any level without the viscosity being impaired.

PU dispersion can be prepared with or without the aid of external emulsifier depending on the structure of PU.<sup>1,2</sup> For PU to be self-emulsifiable, PU should contain hydrophilic segments in its structure. A number of ionic and nonionic compounds have been widely encountered.<sup>3~5</sup> In general, ionic type is stable at high temperature, whereas nonionic type is stable against electrolytes and freezing. Among ionic types, anionic type is preferred over the cationic one, especially for textile applications. Usually 1 wt% of salt group in the PU was proved sufficient to obtain stable dispersion.<sup>6</sup>

Most works with aqueous PU have been done in industrial laboratories,<sup>7~10</sup> and basic data concerning structure-property relationship are sparse in the open literature.<sup>11</sup> This paper describes the preparation of PU ionomers in a prepolymer mixing process. Two types of cycloaliphatic diisocyanate, i. e., isophoron diisocyanate(IPDI) and methylene bis(4-cyclohexyl isocyanate)(H<sub>12</sub>MDI) were used with poly(oxytetramethylene) glycol (PTMG), 1,4-butanediol(BD), and dimethylol propionic acid(DMPA) as potential ionic center. The effect of BD contents and two types of isocyanate on the state of dispersion, and mechanical and viscoelastic properties of emulsion cast film were analyzed.

## EXPERIMENTAL

### Materials

PTMG(M<sub>n</sub>=1000, Hodogaya) and butanediol (BD) were dried and degassed at 80°C, 1~2r-mHg for 5 hrs before use. DMPA(Aldrich) was dried at

100°C for 2 hrs in a drying oven. Extra pure grade of H<sub>12</sub>MDI(Mobay), IPDI (Scholven), and dibutyltin dilaurate(DBT) was used as received. N-methyl-2-pyrrolidone(NMP), triethylene tetramine (TETA), triethylamine(TEA), and solvents used in titration were dried over 3 molecular sieve before use.

### Prepolymer Synthesis

A 500 ml round-bottom, 4-necked separable flask equipped with a mechanical stirrer, thermometer, condenser with drying tube, and a pipette outlet was used as a reactor. Reaction was carried out in constant temperature oil bath. PTMG, DMPA, NMP, and DBT were charged into the dried flask. While stirring, the mixture was heated to 90°C for about 30 min, followed by adding isocyanate(H<sub>12</sub>MDI or IPDI) to the homogenized mixtures. The mixture was reacted at 90°C for about 3 hrs to obtain NCO terminated prepolymers. The change of NCO value during the reaction was followed using a standard dibutylamine back titration method.<sup>12</sup> Upon obtaining the theoretical NCO value, the prepolymers were cooled to 60°C, and triethylamine(TEA)/NMP neutralizing solution was added and stirred for 1 hr while maintaining the temperature at 60°C. Basic formulations of the reaction are given in Table 1.

### Emulsification and Chain Extension

While stirring rapidly, demineralized water was added to the solution to form water dispersion. Aqueous TETA solution 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 product was a stable, over six months at room temperature, urea-urethane dispersion with a solid content about 35 wt%.

### Tests

Particle size and its distribution were measured from Autosizer (Malvern IIC), and state of dispersion was also investigated from transmission electron microscopy(TEM, Hitachi H300). To obtain the micrographs, samples were stained with OsO<sub>4</sub> for 1 week. Tensile properties of the emulsion cast films were measured using an Instron Tensile Te-

**Table 1.** Feed Compositions with the Variation of BD

Sample #	BD(wt%)*	(Unit : g)						
		IPDI	H <sub>12</sub> MDI	PTMG	DMPA	BD	TEA	TETA
PU-I1	0.0	10.881	0.000	25.830	1.333	0.000	1.380	0.965
PU-I2	1.2	11.930	∞	24.225	1.329	0.455	1.380	1.059
PU-I3	2.4	12.945	∞	22.677	1.323	0.906	1.375	1.149
PU-I4	3.6	13.546	∞	21.459	1.320	1.379	1.372	1.262
PU-I5	4.8	15.021	∞	19.547	1.318	1.808	1.370	1.330
PU-H1	0.0	0.000	12.327	24.413	1.332	0.000	1.384	0.927
PU-H2	1.2	∞	13.515	22.681	1.330	0.455	1.381	1.016
PU-H3	2.4	∞	14.690	20.951	1.325	0.909	1.376	1.104
PU-H4	3.6	∞	15.878	19.250	1.324	1.361	1.375	1.194
PU-H5	4.8	∞	17.051	17.540	1.320	1.811	1.372	1.282

\* BD wt% based on prepolymer.

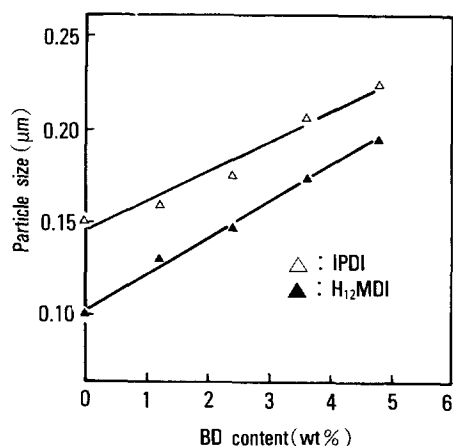
ster at a crosshead speed of 100 mm/min, and an average of at least five measurements was taken to report. Films were prepared by casting the emulsion on a teflon plate, followed by drying at 80°C for 5 hrs. The resulting films were then heated overnight in an oven at 60°C under 2~3 mmHg. Microtensile test specimens were prepared according to ASTM D-1708. Dynamic tests were performed with a Rheovibron (Toyo Baldwin DDV-II) from -100°C to 100°C at 11 Hz with sample, 0.03×0.2×3 cm in size.

## RESULTS AND DISCUSSION

### Effect of BD

In this series of experiments, the content of DMPA was fixed at 3.5 wt% based on prepolymer. Typically in PU, isocyanates and chain extenders form hard domains and polyols form soft domains.<sup>13,14</sup> With more incorporation of chain extender, like DMPA, less polyol is incorporated in the PU structure, which results in the increase of hard segment fraction in PU and urethane linkages. The urethane linkages are capable of hydrogen bondings and augment interchain interactions especially over the ether type polyol (PTMG).

Fig. 1 and 2 show the effect of BD on particle size and its distribution. As noted in the figure, particle size linearly increases with BD. This was



**Fig. 1.** Average particle size as a function of BD.

confirmed from TEM (Fig. 3). As mentioned earlier, the particle size of PU emulsion is primarily governed by the hydrophilicity of PU. However, since the BDs do not actually contribute to the hydrophilicity, unlike DMPA, the change of particle size should be interpreted as a result of structural change of PU with different BD content, i. e., the increased chain rigidity and interchain interactions with BD. It is generally accepted that the ionic centers are predominantly located on the surface of PU particles in water. With the increase of chain rigidity of PU prepolymer, conformational change from homogeneous solution in organic solvent

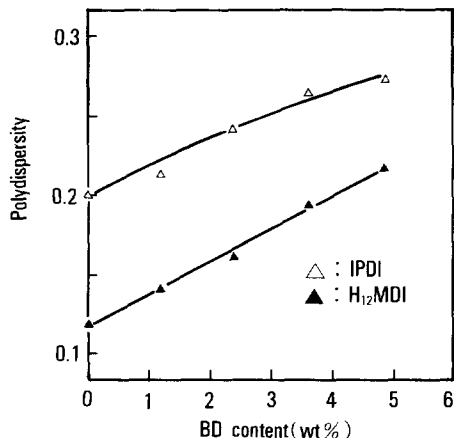


Fig. 2. Distribution of particle size as a function of BD.

(NMP) to micelle structure in water may be less plausible. In addition, rigid particles are less deformable in shear field, and this should give larger particles at the stage of emulsification under shear. Also, the increased interchain interactions between prepolymers should give PU in the solution more cohesive interaction, which is manifested by higher viscosity. With higher viscosity of the dispersed phase, fine breakup should be difficult. During the present experiment, it was observed that prepolymer with high BD content showed rod climbing at the initial stage of emulsification.

With the increase of BD, modulus (Fig. 4) as well as the strength (Fig. 5) of PU film increases, while the elongation at break (Fig. 6) decreases. The results are similar to those of DMPA. BD provides PU with augmented hard fractions and urethane linkages, whereas DMPA gives hydrophilicity and Coulombic force, in addition to the above two. However, the increase of modulus and strength with BD apparently seems more prominent than DMPA. This is due to the inclusion of DMPA (3.5 wt%) in BD experiments.

Regardless of the type of isocyanate, the elastic modulus ( $E'$ , Fig. 7) increases, and the major transition temperature (Fig. 8) moves toward the higher temperature with BD. PTMG as well as the two types of isocyanates used do not crystallize. Therefore, with the increase of BD, accompanied

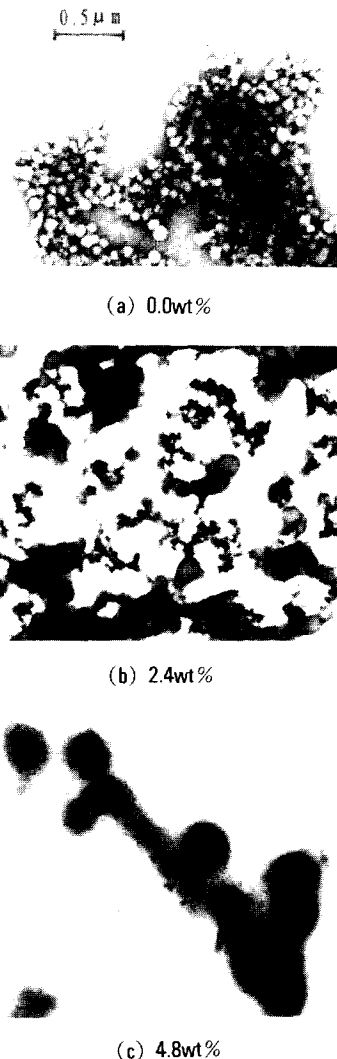


Fig. 3. TEM micrographs of the emulsion with different BD content for IPDI-PTMG system (X30000).

by the increase of hard domains, hard-soft phase mixing should be more plausible. This should lead to the increase of soft  $T_g$ , and the decrease of hard  $T_g$  (not observable because of its low fraction).

**Effect of Isocyanate Type**

Both IPDI and H<sub>12</sub>MDI have extensively been described for use in PU dispersion.<sup>7-8</sup> This primarily is due to their nonyellowing upon exposing to UV. In addition, the stability of cycloaliphatic

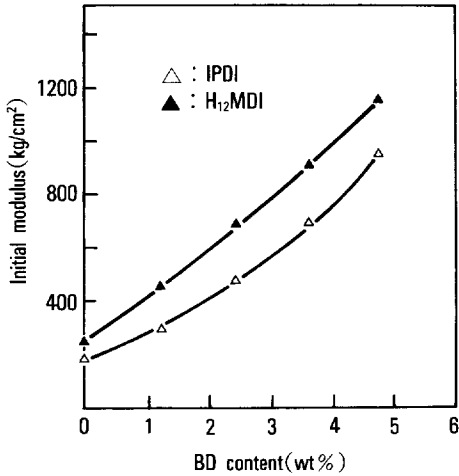


Fig. 4. Initial modulus as a function of BD.

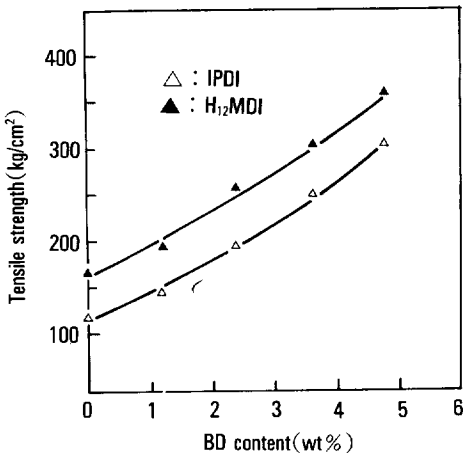


Fig. 5. Tensile strength as a function of BD.

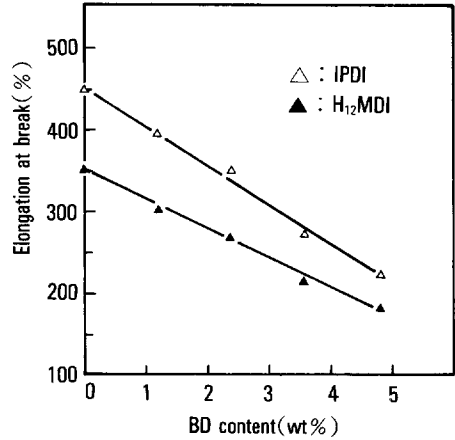


Fig. 6. Elongation at break as a function of BD.

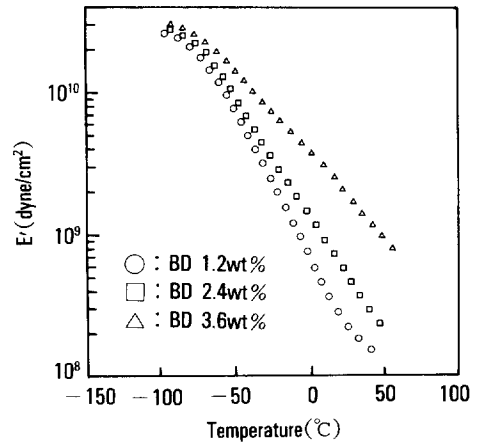


Fig. 7. Effect of BD on storage moduli for PTMG-H<sub>12</sub>MDI system.

type diisocyanate toward water during processing is also of significant account for use in PU dispersion. Particle size and its distribution are smaller and narrower with H<sub>12</sub>MDI than with IPDI (Figs. 1 and 2). Tensile modulus (Fig. 4) and strength (Fig. 5) are higher, and elongation at break (Fig. 6) is lower with H<sub>12</sub>MDI than with IPDI when compared at the same DMPA content. However, the effect of DMPA gives essentially identical trends in both of the PU containing different type of isocyanate. This suggests that the difference in properties between the two types of PU essentially co-

mes from structural difference of the isocyanates. Hard domains containing IPDI as well as H<sub>12</sub>MDI do not crystallize due to their existence of isomers.<sup>15,16</sup> However, H<sub>12</sub>MDI is symmetric, and IPDI is asymmetric. In addition, two NCO group of H<sub>12</sub>MDI are directly attached to cyclohexane ring, and this gives a very cohesive structure of the hard segments. On the contrary, only one of the NCO groups of IPDI is directly attached to the ring, and the other via methylene linkage. The asymmetry and less cohesive structure of IPDI should provide PU with more flexibility and less rigidity as our results indicated (Figs. 3 and 4). The solubility pa-

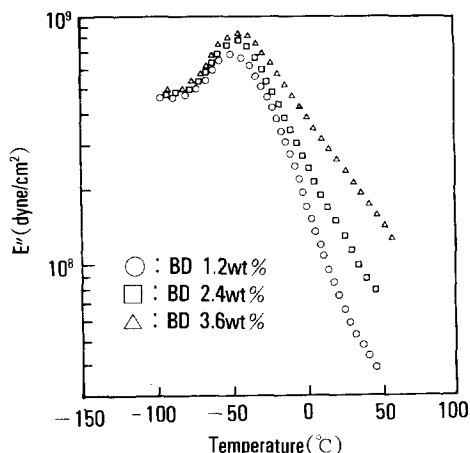


Fig. 8. Effect of BD on loss moduli for PTMG-H<sub>12</sub>MDI system.

parameter of water, H<sub>12</sub>MDI, and IPDI, calculated from group contribution theory,<sup>17</sup> were respectively 24.41, 17.45, 13.27 J<sup>1/2</sup>/cm<sup>3/2</sup>. The solubility parameter of H<sub>12</sub>MDI is closer to that of water, and this would give smaller particle for PU dispersion from H<sub>12</sub>MDI.

## REFERENCES

1. U. S. Patent 2,968,575 (1954) Du Pont.
2. U. S. Patent 3,437,624 (1964) Wyandotte.
3. U. S. Patent 4,408,008 (1983).
4. U. S. Patent 4,237,246 (1980).
5. U. S. Patent 4,238,378 (1980).
6. Ger. Offen. 1,495,745 (1963) Bayer A. G.
7. S. L. Hsu, H. X. Xiao, H. H. Szmant, and K. C. Frisch, *J. Appl. Polym. Sci.*, **29**, 2467 (1984).
8. D. Dieterich, W. Keberle, and H. Witt, *Angew. Chem. Internat. Ed.*, **9**, 40 (1970).
9. H. A. Al-Salah, K. C. Frisch, H. X. Xiao, and J. A. McLean, Jr., *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 2127 (1987).
10. K. Matsuda, H. Ohmura, Y. Tanaka, and T. Sakai, *J. Appl. Polym. Sci.*, **23**, 141 (1979).
11. W. C. Chan and S. A. Chen, *Polymer*, **29**, 1995 (1988).
12. D. J. David and H. B. Staley, "Analytical Chemistry of Polyurethanes", High Polymer Series, XVI, Part III, Wiley-Interscience, New York, 1969.
13. C. Hepburn, "Polyurethane Elastomers", Appl. Sci. Publishers, London, 1982.
14. G. Oertel, "Polyurethane Handbook", Hanser Publishers, 1985.
15. J. W. C. Van Bogart, D. A. Bluemke, and S. L. Cooper, *Polymer*, **22**, 1428 (1981).
16. A. V. Cunliffe, A. Davis, M. Farey, and J. Wright, *Polymer*, **26**, 301 (1985).
17. D. W. Vankrevelen and P. J. Hoftyzer, "Properties of Polymers", Elsevier, New York, Part II, 1976.