

# IPDI계 폴리우레탄 아이오노머 분산 : 채연장제 형태 및 함량이 유화입경 및 Emulsion Cast Film의 물리적 성질에 미치는 영향

김 병 규 · 김 창 기 · 이 영 민 · 정 한 모\*

부산대학교 고분자 공학과 · \*울산대학교 화학과

(1990년 8월 2일 접수)

## IPDI-Based Polyurethane Ionomer Dispersions : Effect of Extender Type and Content on Particle Size and Physical Properties of Emulsion Cast Film

Byung Kyu Kim, Chang Kee Kim, Young Min Lee, and Han Mo Jeong\*

Dept. of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

\*Dept. of Chemistry, University of Ulsan, Ulsan 680-749, Korea

(Received August 2, 1990)

**요 약 :** Isophoron diisocyanate(IPDI), poly(tetramethylene adipate) glycol(PTAd) 및 dimethylolpropionic acid(DMPA) 등으로 부터 polyester polyurethane(PU)을 제조, 이를 triethylamine (TEA)으로 중화시킨후 물로 분산, 수상에서 triethylene tetramine (TETA)으로 채연장 시킴으로써 안정된 수분산성 PU를 제조하였다. 특히 PU 합성과정에서 두 종류의 채연장제(butanediol 및 neopentyl glycol)를 사용, 이들의 함량이 유화입경 및 emulsion cast film의 물리적 성질에 미치는 영향을 검토하였다.

**Abstract :** Isophoron diisocyanate (IPDI)-based polyester polyurethane (PU) dispersion in water were prepared in a prepolymer mixing process. Dimethylol propionic acid(DMPA), triethylamine (TEA), and triethylene tetramine(TETA) were respectively used as potential anionic center, neutralizing agent, and chain extender. Two types of chain extender i. e., butanediol(BD) and neopentyl glycol(NPG), were used in PU forming reactions. The effects of type and extent of chain extension were systematically analyzed in terms of particle size, and physical properties of the emulsion cast films.

### INTRODUCTION

Due mainly to the environmental considerations, aqueous polyurethane (PU) dispersion has recently been widely encountered in coatings and adhesives to textile, leather, and many of the poly-

meric substrates.<sup>1~3</sup> Conventional PU is insoluble in aqueous media, and forms phase separations into large domains. For PU to be dispersible in water, ionic and/or nonionic hydrophilic segments should be incorporated in PU structure.<sup>1~6</sup> Advantages and disadvantages of ionic and nonionic

type PU are well documented in literatures.<sup>7,8</sup>

Works on aqueous PU dispersions have in the past been pioneered by industry laboratories,<sup>3,9~11</sup> and detailed data on particle size and physical properties of emulsion cast films are rarely available in open literature.<sup>12</sup>

We describe the preparations of aqueous PU dispersion from poly(tetramethylene adipate) glycol (PTAd), isophoron diisocyanate (IPDI) with  $\alpha,\alpha'$ -dimethylolpropionic acid(DMPA) as anionic centers. Nonionic hydrophilic segment, i. e., monofunctional ethylene-propylene oxide ether (EOE) was also incorporated. Effects of extender type and content were systematically analyzed in terms of particle size, mechanical, and viscoelastic properties of emulsion cast films.

## EXPERIMENTAL

### Materials

PTAd( $\bar{M}_n=1016$ , Dongsung Chemicals) was dried at 80°C, 0.1 mmHg until no bubbling is observed. Triethylamine was used after treating over 3 Å molecular sieve for 3 days before use. Other extra pure grades of DMPA(Aldrich), triethylene tetramine(TETA, Junsei), N-methyl-2-pyrrolidone (NMP), isophoron diisocyanate(IPDI, Huls AG), butanediol(BD, Junsei), and neopentyl glycol (NPG, Aldrich) were used without further purifications. Extra pure grade of dibutyltin dilaurate (DBT, T-12) was employed as catalyst.

### Procedure

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 temperature oil bath, with  $\pm 0.5^\circ\text{C}$  precision. PTAd, DMPA, BD or NPG, NMP, and DBT(see Table 1 for the formations) were charged into the dried flask while stirring, the mixture was heated to 100°C for about 30 min. Homogenized mixtures were cooled to 65°C, then IPDI was added. The mixture was heated to 90°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. Upon obtaining the theoretical NCO value, the prepolymers were cooled to 65°C, and TEA/NMP neutralizing solution was added and stirred 10 min while the temperature was maintained at 65°C.

While stirring rapidly, demineralized water was added to the solution to form water dispersion. TETA solution dissolved in NMP and water were then fed to the emulsion for a period of 10 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 33%.

### Characterization

Particle size of the dispersion was measured using an Autosizer(Malvern II C) after treating with ultrasonic waves. State of dispersion was also

Table 1. Feed Compositions(unit : g)

Sample #	BD(wt%)	NPG(wt%)	PTAd	DMPA	BD	NPG	IPDI	TEA	TETA
PU-B1	0.0	0.0	26.92	1.050	0.00	0.00	10.444	0.792	0.783
PU-B2	1.2	"	25.34	1.033	0.46	"	11.480	0.780	0.861
PU-B3	2.4	"	24.94	1.083	0.96	"	13.160	0.820	0.987
PU-B4	3.6	"	22.18	1.031	1.38	"	13.636	0.778	1.023
PU-B5	4.8	"	21.58	1.076	1.92	"	15.400	0.821	1.155
PU-N2	0.0	1.2	25.52	1.036	0.00	0.46	11.340	0.781	0.851
PU-N3	"	2.4	24.09	1.034	"	0.96	12.250	0.780	0.920
PU-N4	"	3.6	22.67	1.033	"	1.38	13.160	0.779	0.987
PU-N5	"	4.8	21.15	1.026	"	1.82	14.000	0.774	1.050

wt% : total solid base, DBT : 200 ppm, NMP : 11.5 g, H<sub>2</sub>O : 63 g, solid content : 35 wt%

viewed from transmission electron microscopy (TEM, Hitachi H300). TEM samples were stained with  $\text{OsO}_4$  for 1 week. Mechanical and viscoelastic properties of the emulsion cast films were respectively measured from Instron tensile tester, and Rheovibron (Tokyo Baldwin DDV-II). Tensile tests were made at room temperature following ASTM D-412 with type C specimens. Rheovibron tests were performed from  $-150$  to  $80^\circ\text{C}$  at 11 Hzs. Films were prepared by casting the emulsion on a Teflon plate, followed by drying at  $40^\circ\text{C}$  for 12 hrs. Moisture was further dried off at  $30^\circ\text{C}$ , 20 mmHg for the next 24 hrs.

## RESULTS AND DISCUSSION

### Effects of BD

The effect of BD on particle size and its distribution

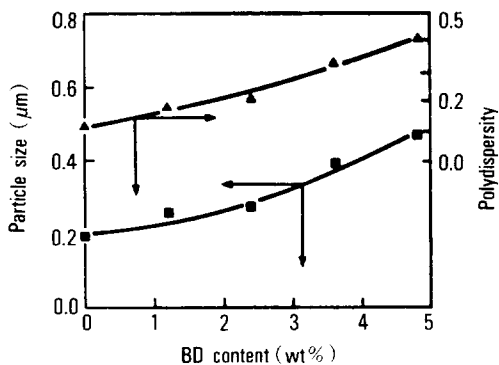


Fig. 1. Average particle size and distribution as a function of BD.

tribution are shown in Fig. 1. It is seen from the figure that the average particle size increases with BD content, and the particle size distribution becomes broader. Typically in PU, diisocyanates and chain extenders form hard segment, and polyols form soft segments.<sup>13,14</sup> As more chain extenders are incorporated in PU structure, PU backbones should become rigid with increased number of urethane linkages. Also, it is reasonably presumed that the nonionic hydrophilic segments as well as anionic centers are predominantly located on the surfaces of PU particles in aqueous media.<sup>15</sup> However, with increased chain rigidity of PU, conformational changes from homogeneous solution in NMP to hydrophobic-hydrophilic spherical structure in water may be less plausible. In addition, rigid particles are less deformable in shear field, and this should lead to larger particle size at the stage of emulsification under shear. The increase of particle size with BD content is also seen in TEM micrographs (Fig. 2).

Moduli (initial and 100% elongation), tensile strength, and elongation at break as a function of BD content are shown in Figs. 3 and 4. As expected, moduli and tensile strength increase with BD content, and elongation at break decrease. Basic structure-property relationships in PU state that hard segments affect hardness and strength, and controlled by the total NCO content.<sup>13</sup> With the increase of BD, NCO content is increased in proportion in stoichiometric reactions.

Viscoelastic properties of the PU as a function

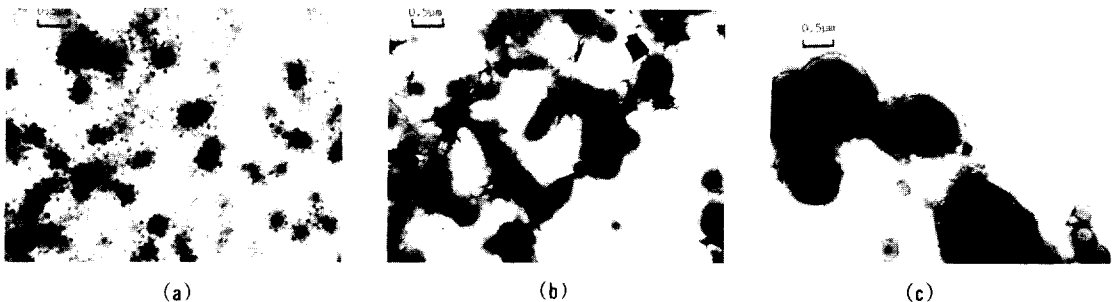


Fig. 2. TEM micrographs of the emulsion with different BD content : (a) 0.0 (B) 2.4 (c) 4.8wt% (X20000).

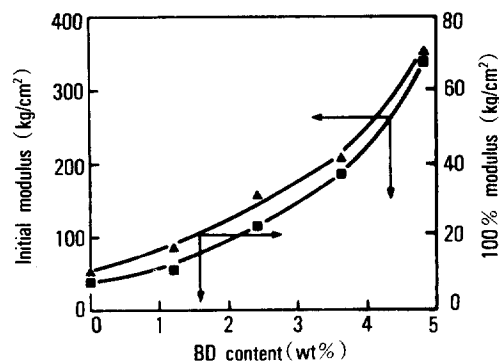


Fig. 3. Initial and 100% modulus as a function of BD.

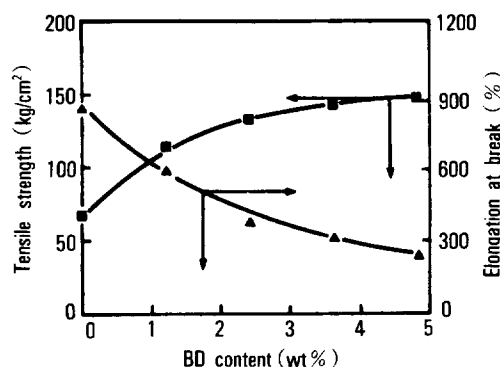


Fig. 4. Tensile strength and elongation at break as a function of BD.

of BD are shown in Figs. 5 and 6. Elastic modulus ( $E'$ ) is directly related to load bearing capability, whereas the viscous component ( $E''$ ) to hysteresis characteristics. Elastic moduli of the present PUs (Fig. 5) are typical of linear amorphous polymers, and the value at room temperature increase as the BD content increase. The trend is consistent with our Instron data. Temperature characteristics of PU are, more and less, governed by the hard/soft segment morphology, which often is obtained by X-ray data. It is seen that the loss peak (Fig. 6) moves toward the higher temperature as the BD content increases, indicative of increased chain rigidity. It may be noted that the peak area also increases with BD contents. Since the loss peak mainly corresponds to amorphous interactions, increased amorphous interactions are also indicated, proba-

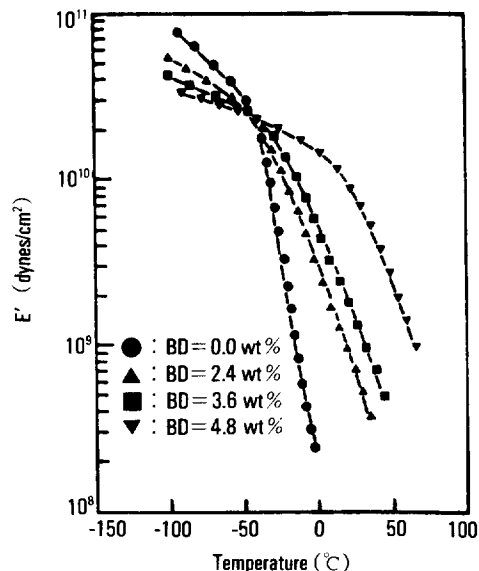


Fig. 5. Effect of BD on storage moduli of films.

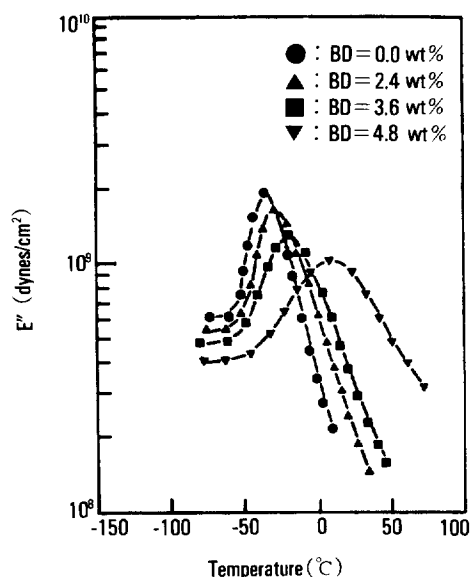


Fig. 6. Effect of BD on loss moduli of films.

bly via the increased number of urethane linkages.

#### Effects of NPG

The effect of NPG on particle size and its distribution are shown in Fig. 7. Particle size increases, and its distribution becomes broader as the NPG

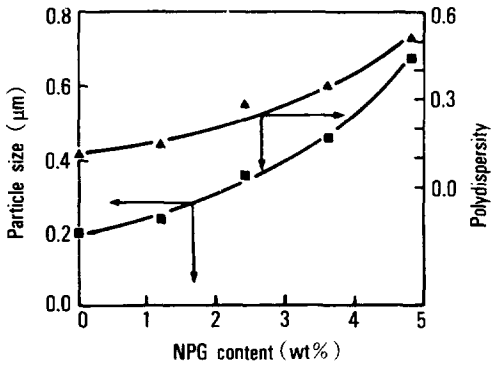


Fig. 7. Average particle size and distribution as a function of NPG.

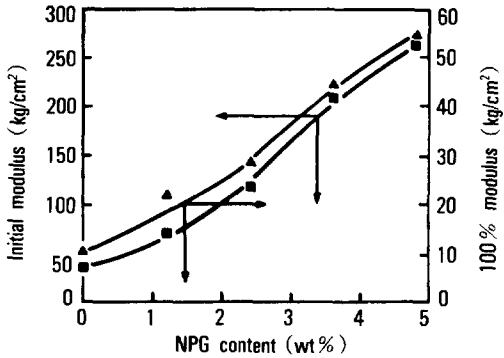


Fig. 8. Initial and 100% modulus as a function of NPG.

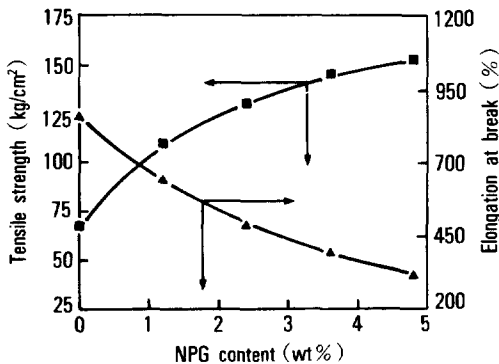


Fig. 9. Tensile strength and elongation at break as a function of NPG.

content increase. The effects are essentially identical with those of BD. However, particle size increase with NPG is a bit more than that of BD. This probably is due to the slight increase in

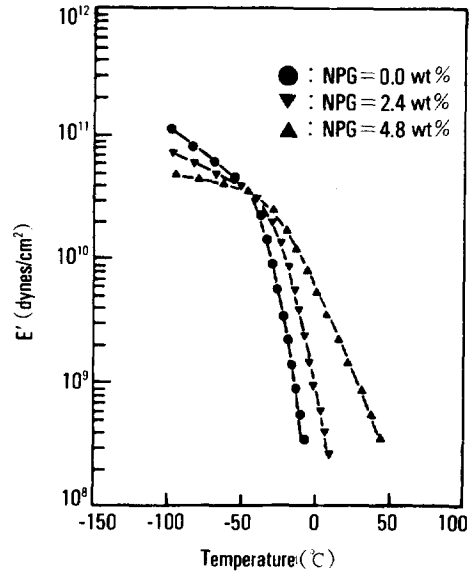


Fig. 10. Effect of NPG on storage moduli of films.

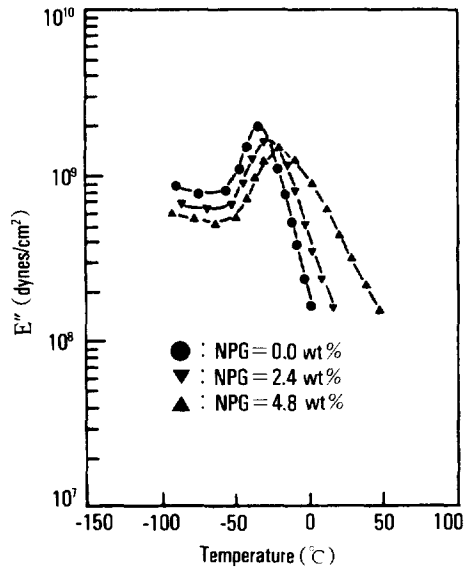


Fig. 11. Effect of NPG on loss moduli of films.

hydrophobic chain segment of NPG over BD, i. e., 3 and 2.

As the NPG content is increased modulus (Fig. 8) and tensile strength are increased, and elongation at break is decreased (Fig. 9). When compared with those of BD, modulus and tensile strength in-

crements are slightly lower for NPG. This probably is due to the short chain branching of NPG.

Viscoelastic properties of NPG extended PUs are shown in Figs. 10 and 11. Elastic modulus increase with NPG content, and loss peak moves toward higher temperatures like in BD extended PU. However, the effects are less pronounced when compared with those of BD.

## REFERENCES

1. J. Wypych, "Polymer Modified Textile Materials", John Wiley & Sons, New York (1988).
2. D. Dieterich and J. N. Riech, *Adhesives Age, Feb.*, 24 (1978).
3. S. L. Hsu, H. X. Xiao, H. H. Szmant, and K. C. Frisch, *J. Appl. Polym. Sci.*, **29**, 2467 (1984).
4. U. S. Patent 4,408,008 (1983).
5. U. S. Patent 4,237,246 (1980).
6. U. S. Patent 4,238,378 (1980).
7. K. C. Frisch and D. Klempner, Eds, "Advances in Urethane Science and Technology", 10, 121 (1987).
8. R. Buscall, T. Corner, and J. F. Stageman, "Polymer Colloids", Elsevier Appl. Sci. Publishers, New York (1985).
9. D. Dieterich, W. Keberle, and H. Witt, *Angew. Chem. Internat. Ed.*, **9**, 40 (1970).
10. H. A. Al-Salah, K. C. Frisch, H. X. Xiao, and J. A. McLean, Jr., *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 2127 (1987).
11. K. Matsuda, H. Ohmura, Y. Tanaka, and T. Sakai, *J. Appl. Polym. Sci.*, **23**, 141 (1979).
12. W. C. Chan and S. A. Chen, *Polymcr.*, **29**, 1995 (1988).
13. C. Hepburn, "Polyurethane Elastomers", Appl. Sci. Publishers, London, 1982.
14. G. Oertel, "Polyurethane Handbook", Hanser Publishers, 1985.
15. O. Lorenz, V. Budde, K. H. Reinmoeller, *Angew. Makromol. Chem.*, **87**, 35 (1980).