

환상 지방족 Isocyanate 및 Polytetramethylene Glycol로 제조한 수성 Polyurethane : 1. 음 Ion 함량이 분산 및 Film 물성에 미치는 영향

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Aqueous Polyurethanes from Cycloaliphatic Diisocyanate and Polytetramethylene Glycol : 1. Effect of Anionic Content on Dispersion and Film Properties

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요 약 : 환상 지방족 isocyanate (methylene bis(4-cyclohexyl isocyanate) (H_{12} MDI) 및 isophoron diisocyanate(IPDI)와, polytetramethylene glycol(PTMG) 및 dimethylol propionic acid(DMPA,쇄연장제)로 부터 polyurethane(PU) ionomer를 제조, 이를 물에 분산시킴으로써 안정된 수성 PU를 제조하였으며, 음 ion center의 함량이 분산 입경 및 emulsion cast film의 물리적 성질에 미치는 영향을 검토하였다. DMPA의 함량이 증가할수록 유화입경은 점근적으로 감소하였으며, 인장 물성(탄성률 및 강도)은 증가하였고, α -완화는 고온으로 이동되었으며 무정영역의 상호인력 역시 증가함을 알 수 있었다. 전반적으로 H_{12} MDI계 PU가 IPDI계 PU에 비해 유화입경이 작고, 기계물성이 우수하게 나타났다.

Abstract : Polyurethane(PU) ionomers were prepared from cycloaliphatic diisocyanate(methylene bis(4-cyclohexyl isocyanate) (H_{12} MDI) and isophoron diisocyanate(IPDI)) and polytetramethylene glycol(PTMG) using an anionic type chain extender, viz. dimethylol propionic acid(DMPA). The effect of ionic content 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 DMPA in PU, particle size of emulsion decreased asymptotically, tensile modulus and strength increased, and the α -transition moved toward the higher temperature with more amorphous interactions. With regard to the structural effect of the isocyanate, H_{12} 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 is occurred 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.^{1,2} 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.^{3~5} 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 proved sufficient to obtain stable dispersion.⁶

Most works with aqueous PU have been done in industrial laboratories,^{7~10} and basic data concerning structure-property relationship are sparse in the open literature.¹¹ 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) (H₁₂MDI)

were used with poly(oxytetramethylene) glycol (PTMG), and dimethylol propionic acid(DMPA) as potential ionic center. The effect of DMPA and two types of isocyanate on the state of dispersion, and mechanical and viscoelastic properties of emulsion cast film were analyzed.

EXPERIMENTAL

Materials

PTMG(Mn=1000, Hotogaya) was dried and degassed at 80°C, 1~2mmHg for 5 hrs before use. DMPA(Aldrich) was dried at 100°C for 2 hrs in drying oven. Extra pure grade of H₁₂MDI(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 Å molecular sieve before use.

Preparation of PU Emulsion

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 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(H₁₂MDI or IPDI) to the homogenized mixtures. The mixture was heated to 90°C for about 3 hrs to obtain NCO termina-

Table 1. Feed Compositions(unit : g)

Sample #	DMPA(wt %)	IPDI	H ₁₂ MDI	PTMG	DMPA	TEA	TETA
PU-I1	1.5	9.888	0.000	28.209	0.580	0.421	0.877
PU-I2	2.5	10.378	0.000	27.001	0.957	0.722	0.921
PU-I3	3.5	10.881	0.000	25.830	1.333	1.001	0.965
PU-I4	4.5	11.343	0.000	24.654	1.697	1.279	1.006
PU-I5	5.5	11.832	0.000	23.519	2.058	1.553	1.050
PU-H1	1.5	0.000	11.221	26.920	0.581	0.437	0.884
PU-H2	2.5	0.000	11.769	25.639	0.959	0.723	0.884
PU-H3	3.5	0.000	12.327	24.413	1.332	1.004	0.927
PU-H4	4.5	0.000	12.868	23.185	1.696	1.281	0.967
PU-F5	5.5	0.000	13.401	21.978	2.059	1.552	1.008

DMPA wt% based on prepolymer.

ted prepolymers. The change of NCO value during the reaction was determined using a standard dibutylamine back titration.¹² Upon obtaining the theoretical NCO value, the prepolymers were cooled to 60°C, and triethylamine(TEA)/NMP neutralizing solution was added and stirred for 10 min while maintaining the temperature at 60°C. Basic formulations of the reaction are given in Table 1. 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 product was a stable, over six months at room temperature, urea-urethane dispersion with a solid content about 35%.

Testing Method

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 OsO₄ for 1 week. Tensile properties of the emulsion cast films were measured using an Instron Tensile Tester 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 50°C at 11 Hz with sample, 0.03 × 0.2 × 3 cm in size.

RESULTS AND DISCUSSION

Effect of DMPA

It is of practical importance to be able to control the average particle size and its distribution of PU dispersion. For example, relatively large particle is preferred in many of the surface coatings for rapid drying, and relatively small one is desirable when

the deep penetration of dispersion into the substrate is an essential step. Fig. 1 shows the average particle size and its distribution as a function of DMPA content. It is seen that the particle size decreases with increasing DMPA, both in IPDI and H₁₂MDI systems. The Autosizer result was visually confirmed from TEM(Fig. 2). In PU dispersion, average size of particle is, more and less, controlled by the mixing conditions such as rpm and temperature. However, it is mostly governed by the hydrophilicity of the PU. DMPA is hydrophilic in nature, and reduces particle size, effectively at low

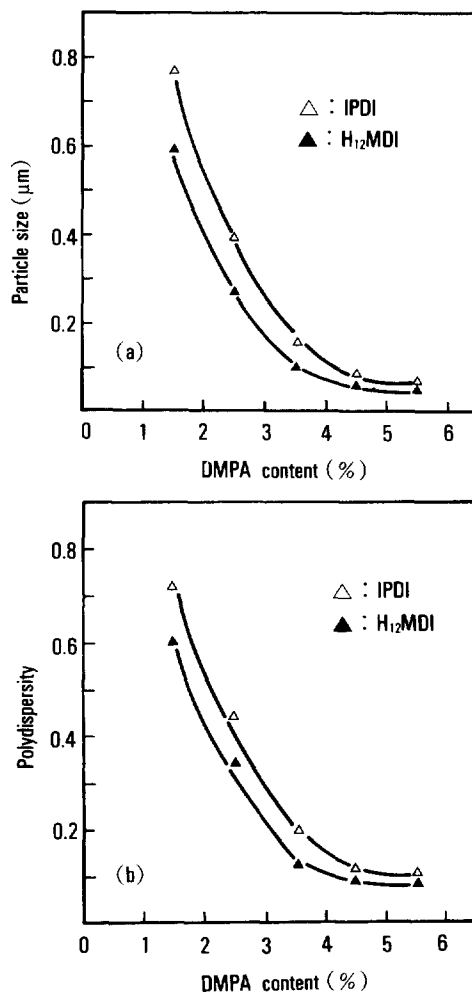


Fig. 1. Average particle size(a) and its distribution(b) as a function of DMPA.

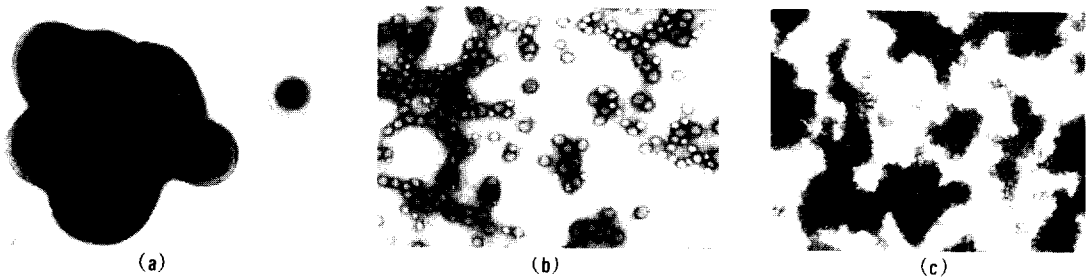


Fig. 2. TEM micrographs of the emulsion with different DMPA content for PTMG-H₁₂MDI system : (a) 1.5 (b) 3.5 (c) 5.5wt% (X30000).

and asymptotically at high content. The asymptotic behavior is probably due to the increase of viscosity with DMPA. Ionic type PU dispersion is stabilized by diffusing electrical double layer formation by the salt groups.¹³ The reduction of particle size with more DMPA should augment the total double layer and hydrodynamic volume of the particle as well, leading to an increase of viscosity.¹⁴ This gives difficulty in breakup of dispersed phase, and an asymptotic behavior shown in the figure is expected.

The mechanical properties of emulsion cast films are shown in Figs. 3 to 5. While the modulus and tensile strength increase, elongation at break decreases as DMPA content increases. Typically in PU, polyols form soft domain, and isocyanates and urethane linkages form hard domain. As the content of DMPA increases, less amount of polyol soft segment, and more amount of urethane linkages are incorporated in the PU structure. Moreover, ionic centers are source of Coulombic force and hydrogen bonding which together contribute to the increased interchain interactions.^{15~23} This supports the increase in the modulus and tensile strength with increasing amount of DMPA. The decreased ductility of the PU with DMPA is mainly due to the increased rigidity as the soft domain fraction decreases.

Viscoelastic properties of the PU are shown in Figs. 6 and 7. The storage modulus(E') increased with DMPA, below and above T_g (Fig. 6). It is also seen that the effect of DMPA is much more pro-

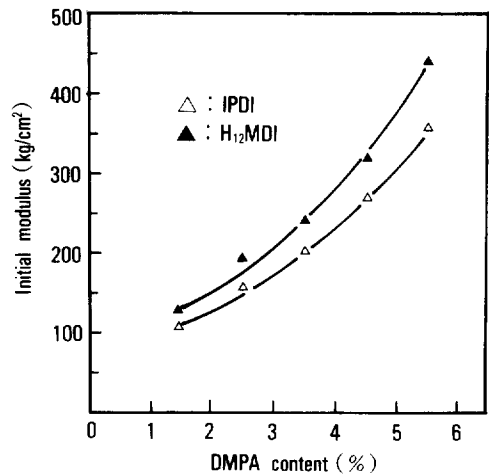


Fig. 3. Initial modulus as a function of DMPA.

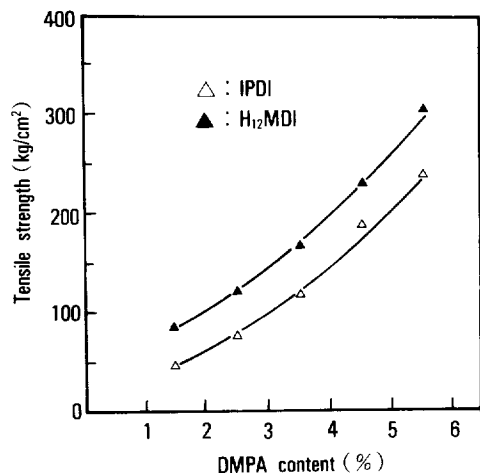


Fig. 4. Tensile strength as a function of DMPA.

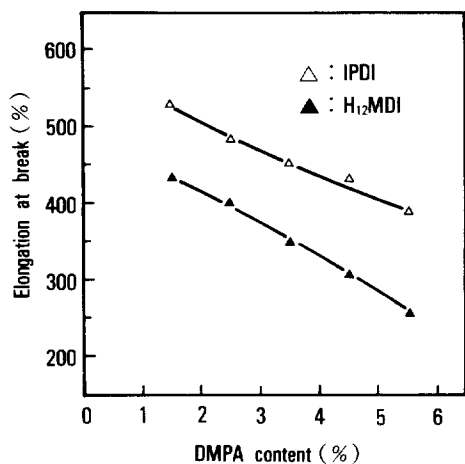


Fig. 5. Elongation at break as a function of DMPA.

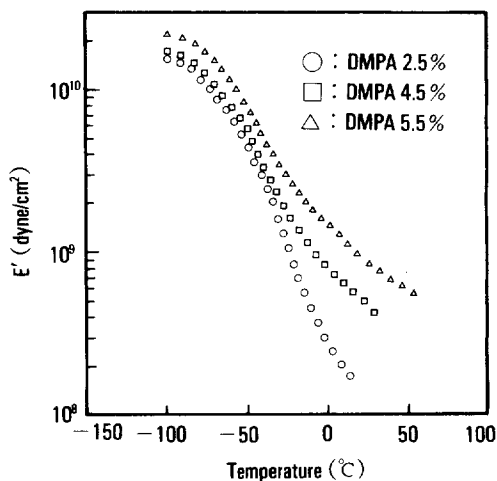


Fig. 6. Effect of DMPA on storage moduli of PTMG- H_{12} MDI system.

nounced in rubbery state than in glass state. This is an indication that the ionic force, in addition to the increased number of urethane linkage, significantly contribute to the elastic properties of the PU. With more DMPA incorporation, the glass transition temperature(T_g) also increases(Fig. 7), a result consistent with modulus increase. Increase in T_g may mainly be caused from hard fraction increase. However, when the area of loss peak is considered together, it may be concluded that the increased number of ionic centers gave more am-

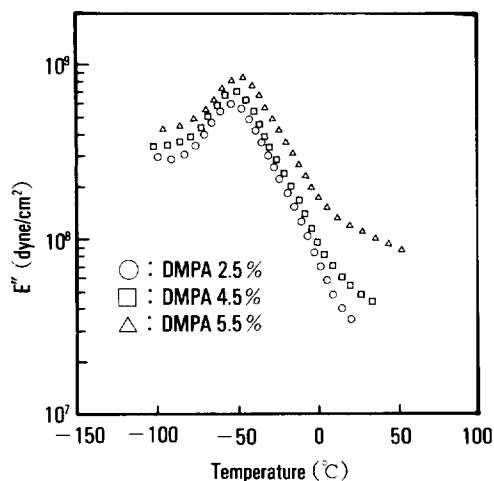


Fig. 7. Effect of DMPA on loss moduli of PTMG- H_{12} MDI system.

orphous interactions, as expected.

Effect of Isocyanate Type

Both IPDI and H_{12} MDI have extensively been described for use in PU dispersion.^{7,8} This primarily is due to their nonyellowing upon exposing to UV. In addition, the stability of cycloaliphatic 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_{12} MDI than with IPDI(Figs. 1). Tensile modulus(Fig. 3) and strength(Fig. 4) are higher, and elongation at break(Fig. 5) is lower with H_{12} 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 comes from structural difference of the isocyanates. Hard domains containing IPDI as well as H_{12} MDI do not crystallize due to their existence of isomers.^{24,25} However, H_{12} MDI is symmetric, and IPDI is asymmetric. In addition, two NCO group of H_{12} 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 to 5). The solubility parameter of water, IPDI, and H_{12} MDI, calculated from group contribution theory,²⁶ were respectively 13.89, 8.09, 8.48. Though not sufficient, slightly closer value of H_{12} MDI over the IPDI to water may be in line with the smaller particle size.

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