

Segmented Polyurethane Ionomer에서 Polyol 종류 및 조성의 영향

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Effect of Polyol Type and Composition in Segmented Polyurethane Ionomers

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요 약 : 환상 지방족 isocyanate인 isophorone diisocyanate(IPDI)와, poly(tetramethylene adipate) glycol(PTAd), polypropylene glycol(PPG), dimethylol propionic acid(DMPA)로부터 polyurethane (PU) ionomer를 제조, 이를 물에 분산시킴으로써 안정된 수성 PU를 제조하였으며, polyol 종류 및 조성이 유화특성 및 emulsion cast film의 열적, 기계적 성질에 미치는 영향을 검토하였다. PTAd 함량이 증가할수록 유화입경은 점근적으로 감소하였으며, 점도, soft segment T_g 및 인장 거동은 증가하는 경향을 나타냈다.

Abstract : Segmented polyurethane(PU) ionomers were prepared from cycloaliphatic diisocyanate, i. e. isophorone diisocyanate(IPDI), poly(tetramethylene adipate) glycol(PTAd), and polypropylene glycol(PPG) using anionic chain extender, viz. dimethylol propionic acid(DMPA). The effect of composition of soft segment on the emulsion properties, and thermal and mechanical properties of emulsion cast film were investigated using Autosizer, Brookfield Viscometer, DSC, and Instron. With more incorporation of PTAd, particle size decreased monotonically, whereas emulsion viscosity, T_g of soft segment, and tensile properties increased.

INTRODUCTION

Physical properties of polyurethane(PU) depend on the type and content of soft and hard segments.¹ Diisocyanates and chain extenders form hard domains, and these mainly affect mechanical proper-

ties at elevated temperature.² Soft segments, viz. polyols affect low temperature properties and chemical resistance, which are controlled by the type and molecular weight of polyols.²⁻⁴ Due mainly to the strong interchain interactions of ester linkage, ester polyols provide PU with good tensile stre-

ngth and thermal stability,⁴ in addition to oil/solvent and oxidation resistance. However, ester polyols are subject to the poor resistance to hydrolysis.^{5,6} On the contrary, ether polyols in PU impart the outstanding resistance to hydrolysis and fungus along with good low temperature properties.^{5,6} The drawbacks of polyether polyol include poor high temperature properties and poor UV resistance of thin films.

We prepared PU from polypropylene glycol (PPG), poly(tetra-methylene adipate) glycol (PTAd), and dimethylol propionic acid(DMPA), together with isophorone diisocyanate(IPDI). By neutralizing the DMPA with triethylamine(TEA), PU ionomer was obtained. The effects of type and composition of soft segments on particle size and viscosity of emulsion, thermal behavior, and mechanical properties of the emulsion cast film were examined.

EXPERIMENTAL

Materials

PPG($M_n=1000$, Korea Polyol Co. Ltd.) and PTAd($M_n=1016$, Dongsung Chemicals) were dried at 80°C under 0.1 mmHg until no bubble was observed. TEA was used after treating over 3Å molecular sieve for 3 days. Other extra pure grades of DMPA(Aldrich), triethylene tetramine(TETA, Junsei Chemical), N-methyl-2-pyrrolidone(NMP), and IPDI(Huls AG) were used without further purification. Extra pure grade of dibutyltin dilaurate(DBT, T-12) was employed as a catalyst.

Procedure

The content of DMPA and IPDI were fixed at 3, 5 and 24 wt% based on total solid, respectively. Total amount of polyol added was about 68% on the solid base, and 5 different polyol mixtures (PPG/PTAd=100/0, 75/25, 50/50, 25/75, 0/100) were employed. 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 the reactor. Reaction was carried out in a constant temperature oil bath. Poly-

ols, DMPA, DBT(200 ppm based on total solid), and NMP(solvent)(3wt% based on total emulsion) were charged into the dried flask. While stirring, the mixture was heated at 90°C for about 30 min, followed by adding IPDI to the homogenized mixture. The mixture was heated for 3 hr to obtain NCO-terminated prepolymers. The change of NCO value during the reaction was determined using a standard dibutylamine back titration.⁷ Once the theoretical NCO value is reached, the prepolymers were cooled to 60°C. TEA was added and the mixture was stirred for 1 hr while maintaining 60°C.

While stirring rapidly, demineralized water was added to the solution to form water dispersion. Chain extension reaction using TETA was carried out for the next 2 hrs with mild agitation.

Characterizations

Average particle size of the dispersion was measured using an Autosizer(Malvern II C) after treating the samples with ultrasonic waves. The dispersion viscosity at 25°C was measured using Brookfield viscometer(DV-1, LV type). PU films were cast from emulsion on a Teflon plate and dried at 80°C for 5 hrs. The remaining moisture was removed at 60°C under 20 mmHg overnight. Thermal properties of the films were determined from differential scanning calorimetry(DSC, Du Pont 910), and mechanical properties of films were measured using an Instron tensile tester with a crosshead speed of 200 mm/min.

RESULTS AND DISCUSSION

Particle Size

Fig. 1 shows that particle size increases monotonically with PPG, i. e., from 0.05(100% PTAd) to 0.28 μm (100% PPG) at the same solid content(30%). In aqueous dispersion of PU ionomer, the particle size decreases with PU hydrophilicity, which is governed primarily by the ionic content.⁴ However, the ionic content was fixed at 3.5wt% throughout the experiments, and hence the change of particle size with PPG content should come from the temperature sensitive hydrophilicity of poly-

ther polyol.⁵ PPG is more hydrophilic than PTAd at room temperature, however loses its hydrophilicity at elevated temperature, almost completely at about 65°C. Therefore, at the stage of emulsification(50°C) PPG was less hydrophilic than PTAd, which led to the increased particle size with PPG content, as in Fig. 1.

Emulsion Viscosity

Fig. 2 shows the emulsion viscosity vs. soft segment composition, where a linear decrease of viscosity with PPG is observed. The viscosity of emulsion depends on a number of factors, such as particle concentration, particle size, particle size distribution, and particle-particle interactions as well as on shear rate of emulsification stage.^{9~11} Generally, larger particle with broad size distribution and smaller interparticle interactions(Coulombic, electrical double layer etc.) lead to lower emulsion viscosity. Since the solid concentration and ionic content are constant, the viscosity rise with PTAd content should directly comes from the particle size reduction with PTAd. With smaller particle, the total hydrodynamic volume will increase to give the increased viscosity.

Thermal Properties

In PPG, the pendant methyl groups disturb chain fit, and hence the PPG segments in PU do

not crystallize.¹² On the contrary, depending on the molecular weight of polyol and crosslink density of PU, PTAd segment is crystallizable. In the present series of experiments, the prepolymer molecular weight was fixed at 4000, and T_m (about 45 °C) of soft segment was observed at 25/75 and 0/100 composition.

The T_g of PPG and PTAd in PU was -42°C and -39.4°C, respectively, and in the PU from mixed polyols, T_g of the soft segment increased monotonically with PTAd content(Table 1), and Fox equation¹³(given below) closely fitted the experimental value.

$$\frac{1}{T_g} = \frac{W_1}{T_{g,1}} + \frac{W_2}{T_{g,2}}$$

where W_i and $T_{g,i}$ respectively designate the

Table 1. Lower T_g of Emulsion Cast Films

composition (PPG/PTAd)	T_g (°C)	
	experimental	Fox equation
100/0	-42.8	-42.8
75/25	-41.7	-42.0
50/50	-41.2	-41.1
25/75	-40.2	-40.3
0/100	-39.4	-39.4

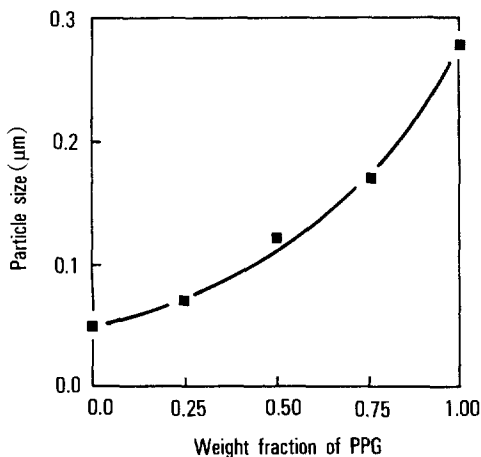


Fig. 1. Average particle size of PU ionomer as a function of PPG fraction.

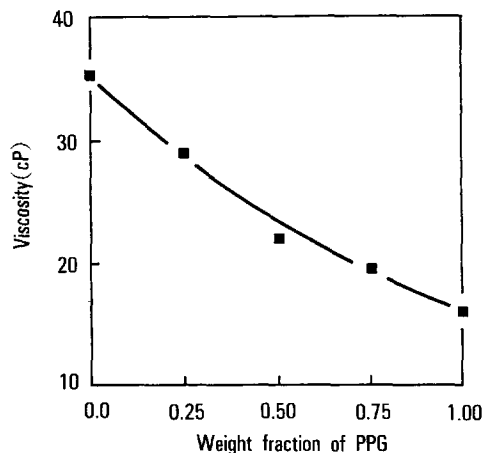


Fig. 2. Emulsion viscosity of PU ionomer as a function of PPG fraction.

weight fraction and T_g of each polyol segment.

Mechanical Properties

Tensile modulus, strength and elongation at break are shown in Fig. 3 to 6. As expected, modulus(except at 100% elongation value), tensile strength, and elongation decrease with PPG, due probably to the decreased interchain interaction.¹² Interchain interactions, such as the hydrogen bonding are much stronger with ester type than with ether type polyol.^{14,15} It is noted that modulus inc-

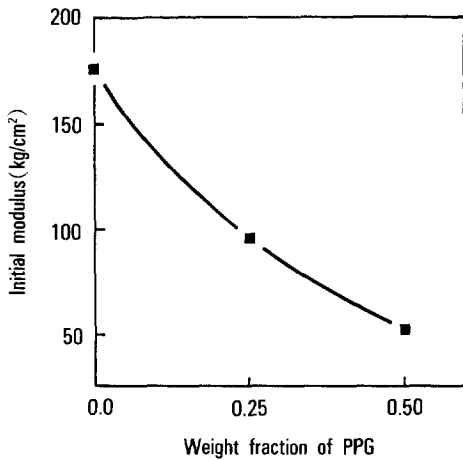


Fig. 3. Initial modulus of PU ionomer as a function of PPG fraction.

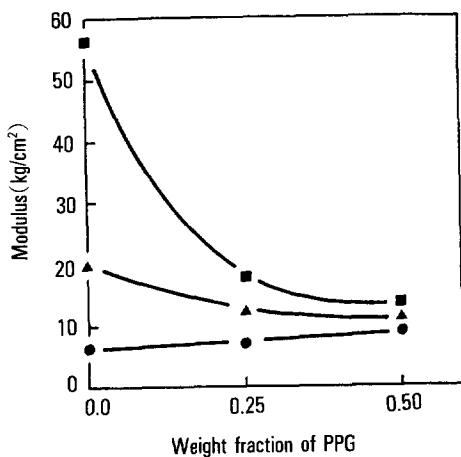


Fig. 4. Tensile modulus of PU ionomer as a function of PPG fraction (● : at 100% elongation, ▲ : 300%, ■ : 500%).

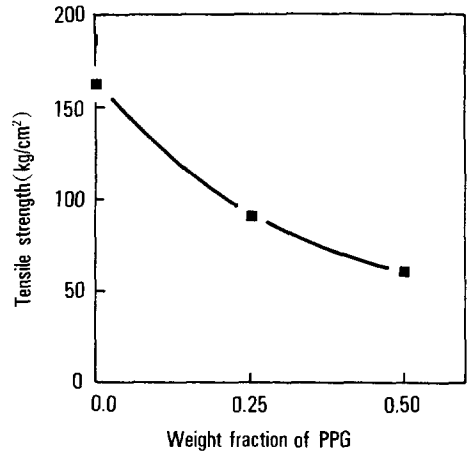


Fig. 5. Tensile strength of PU ionomer as a function of PPG fraction.

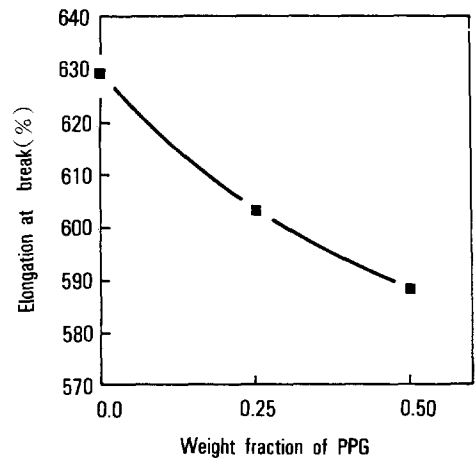


Fig. 6. Elongation at break of PU ionomer as a function of PPG fraction.

reases with elongation(except initial), indicative of strain hardening(Fig. 4). Strain hardening effect is most pronounced with PTAd. This implies that PTAd PUs are strain crystallizable. During the tensile experiment, stress whitening was observed with PTAd PU.

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