

Emulsion Blends of Polyurethane Ionomers from Ester and Ether Type Polyols

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Ester 및 Ether형 Polyol Polyurethane Ionomer의 Emulsion 블렌드

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Abstract: Two types of polyurethane(PU) ionomer dispersion having different type of soft segment, viz. poly(tetramethylene adipate) glycol(PTAd), and polypropylene glycol(PPG) were emulsion blended. Viscosity of emulsion blend, mechanical, and surface properties of the emulsion cast films were determined as a function of blend composition. Mechanical properties showed a large scatter of data or negative deviation from the additivity rule, and this was attributed to the incompatibility of soft segments. Contact angle measurement indicated that air facing surface of emulsion cast film contained more of PPG PU, due probably to its smaller particle diameter compared to PTAd PU.

요 약: Soft segment가 각각 ester 및 ether형 polyol로된 2종의 polyurethane(PU) ionomer를 emulsion 블렌딩하여, 블렌드의 분산정도, 및 emulsion cast film의 점축각, 기계적 특성을 조성의 함수로 측정하였다. 블렌드의 기계물성은 혼합법칙으로부터 심한 scattering이나, negative deviation을 보였으며, 이는 ester 및 ether형 polyol간의 상용성의 결여에 기인하는 것으로 보았다. 점축각 측정 결과로부터 유화입경이 작은 PPG PU 입자가 주로 도막표면층을 형성하는 것을 확인할 수 있었다.

1. Introduction

Polyurethane(PU) ionomer contains ionic groups in its molecular structure, and shows excellent mechanical properties due to the presence of interchain Coulombic forces and hydrogen bondings[1~3].

The ionic groups are hydrophilic in nature and distributed within the large hydrophobic chain segments. This unique structure leads to self-emulsification of PU ionomers in aqueous media. The fact that the PU ionomers can be utilized in the form of water

dispersion take significant advantages over the solvent-based PU. Aside from the cost and solvent emission, PU dispersion can be incorporated into other dispersions[4~6], which is not simply possible with solvent based ones. Blends of PU dispersions with aqueous systems like poly(vinyl acetate), poly(vinyl alcohol), or natural latex gives upgraded adhesive properties to the non-urethane dispersions.

This paper considers the emulsion blends of PU ionomers having different types of soft segments, i. e., poly(tetramethylene adipate) glycol(PTAd) and

poly(propylene glycol)(PPG). In general, soft segments affect low temperature properties and chemical resistance, which are controlled by the type and molecular weight of polyol[1]. Ester based PUs are considered for good tensile strength, thermal stability, and oil/oxidation resistance[2]. Poor hydrolysis resistance due to the ester linkage is the major drawbacks. On the contrary, ether type polyol when incorporated into PU impart outstanding hydrolysis and fungus resistance along with excellent low temperature properties and resilience. Polyether drawbacks include poor UV and oil resistance, and poor high temperature properties[2]. It is expected that the emulsion blends of the two types of ionomers might, more or less, give balanced properties as desired.

2. Experimental

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

Urethane forming reaction was carried out in a 500ml round-bottom, 4-necked separable flask with a mechanical stirrer, thermometer, condenser with drying tube, and a pipette outlet. Reaction was carried out in constant temperature oil bath. PTAd or PPG, DMPA, NMP, and DBT were charged into the dry flask. While stirring, the mixture was heated to 80°C for about 30min, followed by adding IPDI to the homogenized mixtures. Then the mixture was heated to 80°C for about 3 hrs to obtain NCO terminated prepolymers. The change of NCO value during the reaction was determined by using a standard

dibutylamine back titration method[7]. 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. 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. Soft/hard compositions were respectively 62/38 by weight for PTAd based, and 56/44 for PPG based PU.

Particle size of the dispersion was measured using an Autosizer(Malvern II C). Viscosities of emulsion at 25°C were measured using Brookfield viscometer (DV-1, LV type).

PU films were obtained from casting the 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. Contact angle(Erma G-1) at room temperature was measured by dropping water (50 μ l) on film. Mechanical properties of the films were measured using an Instron Tensile Tester at a crosshead speed of 200 mm/min.

3. Results and discussion

3.1. Viscosity

The viscosity of emulsion is of theoretical as well as practical importance in application. Over one hundred theoretical predictions have become available, and these have been reviewed in Rutgers[8], Kim [9], and Saunders[10]. Factors affecting emulsion viscosity include concentration, size, distribution, geometry, and interactions of the particles, in addition to the temperature and shear rate at the emulsification stage.

Average particle size and emulsion viscosity vs. solid content for the PTAd and PPG based PU emulsions are given in Table 1, and the viscosity-composition relationship of the emulsion blends is shown in Fig. 1. Viscosity of PPG based PU emulsion is over several orders of magnitude higher than

that of PTAd based one. It is generally agreed that emulsion of larger particle and broader distribution gives lower viscosity. The average particle size of PTAd PU is slightly larger than that of PPG PU. Though this is in line with the larger viscosity for PPG PU, the particle size difference seems insufficient to explain such big difference in viscosity.

PU ionomer is stabilized via electrical double layers[3], i. e., the anionic centers preferentially covering the particle surface is covered with ammonium counter ions. Ionic contents in PTAd PU and PPG PU were 3.5 and 5.5 wt%, respectively. Therefore it seems reasonable to assume that the Coulombic interactions between the double layers of different

particle is greater for PPG PU, and this would give larger viscosity[11]. This effect is often referred to as electroviscous effect[1].

The blend viscosity(Fig. 1) shows negative deviation from the simple additive rule(dotted line in the figure), except at the two extreme compositions. Negative deviation is probably due to the difference in particle size leading to bimodal or broader particle size distribution[9]. Though not properly applicable to the present system, when two emulsions with different particle size are blended, the finer particles behave as a fluid toward the coarser particle, and exert dilution effect.

Table 1. Particle Size and Emulsion Viscosity of PUs at Various Solid Content

particle size	PTAd based PU	PPG based PU
	0.17 μm	0.14 μm
viscosity(cP)		
at 35wt%	8.1	5800
30wt%	6.3	250
25wt%	4.5	4.0
20wt%	3.7	1.5
15wt%	3.5	0.8

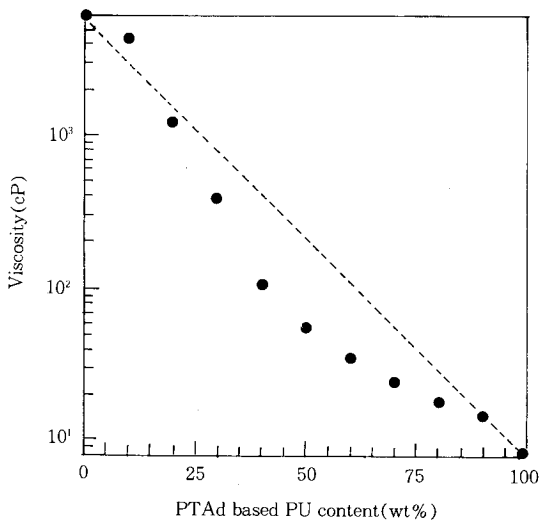


Fig. 1. Emulsion viscosity of the blend vs. composition at 20°C.

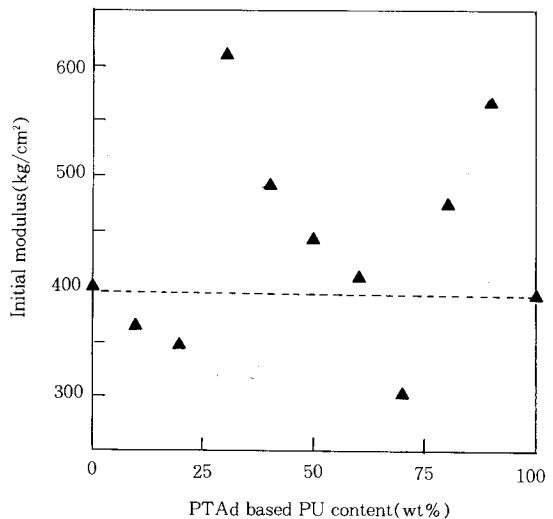


Fig. 2. Initial modulus of the blend vs. composition at 20°C.

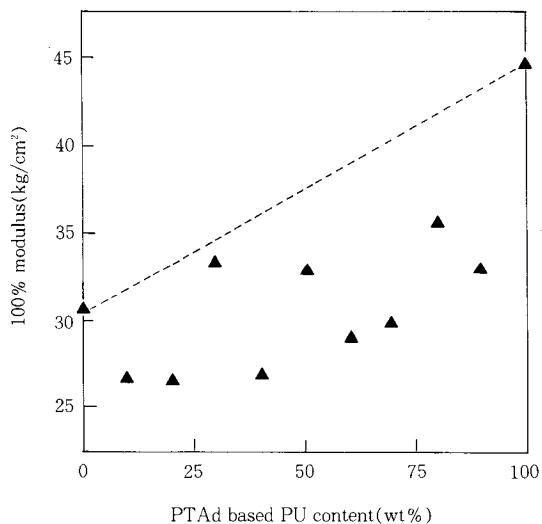


Fig. 3. 100% modulus of the blend vs. composition at 20°C.

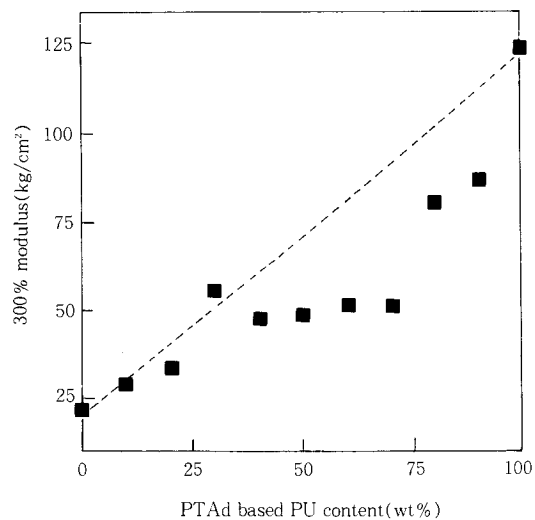


Fig. 4. 300% modulus of the blend vs. composition at 20°C.

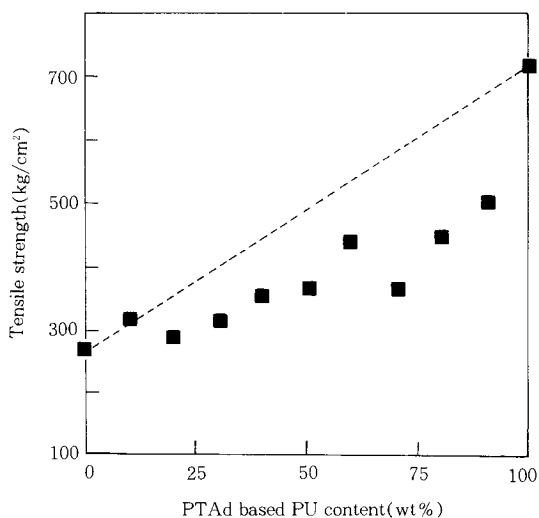


Fig. 5. Tensile strength of the blend vs. composition at 20°C.

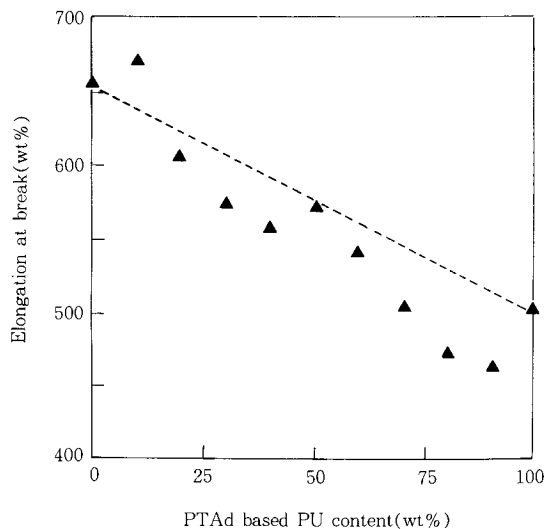


Fig. 6. Elongation at break of the blend vs. composition at 20°C.

modulus shows a serious scatter of data due probably to the incompatibility of the blends. As the strain is increased, the modulus of PTAd PU becomes significantly greater than that of PPG PU, and the blend modulus shows a negative deviation from the additivity, indicating the incompatible nature of the blends. The two types of PU are different only in

their soft segment. Therefore, it is expected that when these two PUs are blended together, hard segments may form a single phase, and repulsion may exist between PTAd and PPG polyols. Tensile strength increases, and elongation at break decrease with the PTAd PU, and generally a negative deviation is dictated as in the modulus trend.

3. 3. Surface and swelling properties

The contact angle vs. composition is shown in Fig. 7. The contact angle with water is unchanged up to 80% PTAd PU. This indicates that air facing surface is mainly composed of PPG PU, which is relatively small in particle diameter. It is plausible that larger particle precipitates rapidly during the process of water evaporation.

Water swell resistance and hydrolytic stability is favored with ether type polyol, and decreases with increasing amount of internal emulsifier. Water swell of the films is shown in Fig. 8. Water swell of PPG PU is smaller than PTAd PU, however, the difference is insignificant due probably to the larger ionic center of PPG PU(5.5 wt%) over the PTAd PU(3.5wt%). For the blends, the water swell is significantly increased, and this may imply that the microstructure of PU film has become coarser upon blending, and it is again an indication of incompatible nature of the blends, especially in soft segments.

Toluene swell of PPG PU is significantly higher than PTAd PU, as expected. For the blends, slightly positive and negative deviation from the additivity rule are seen in PPG and PTAd rich blends. However, the deviation is much smaller compared to the water swell.

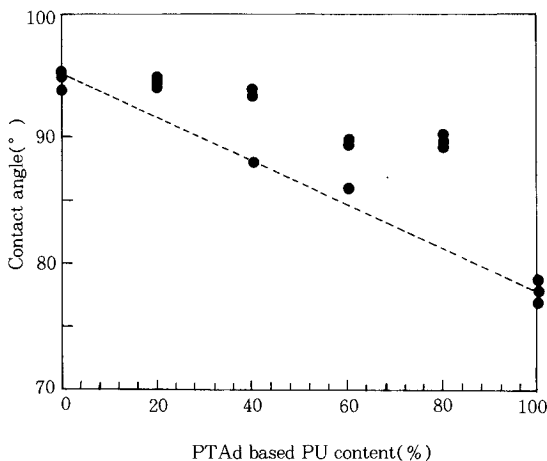


Fig. 7. Contact angle with water vs. composition at 20°C.

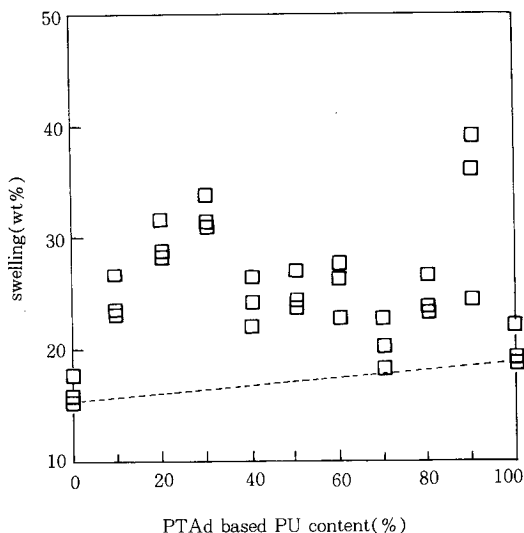


Fig. 8. Degree of swelling vs. composition in water (at 20°C).

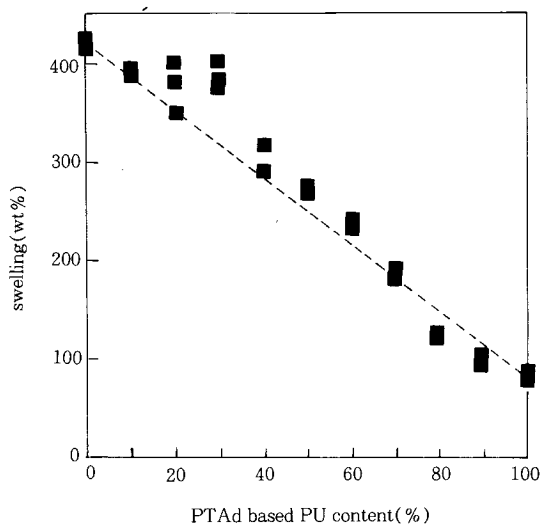


Fig. 9. Degree of swelling vs. composition in toluene (at 20°C).

4. Conclusion

The emulsion blends of PTAd based PU and PPG based PU generally showed negative deviation or large scatter of mechanical data from the simple additivity rule of mixture, due mainly to the incompatible nature of the two types of PU. The air facing

surface of the emulsion cast film contained more of PPG PU, which is smaller in particle size. Swell in water and oil generally increased over the additivity, which again suggests the incompatibility, especially in soft domains.

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