

## Effects of NCO/OH Ratios on Physico-Mechanical Properties of Polyurethane Dispersion

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**Abstract:** A series of water dispersion polyurethanes (PUDs) were prepared by polyaddition reaction using isophorone diisocyanate (IPDI), toluene diisocyanate (TDI), poly(oxytetramethylene) glycol (PTMG), dimethylol propionic acid (DMPA) and poly(oxypropylene) poly(oxyethylene) triol (FA-703). The effect of NCO/OH molar ratio on the physico-mechanical properties of the polyurethanes were characterized by particle size analyzer, viscosity, tensile tester, DSC and molecular weight. IR spectroscopy was used to check the end of polymerization reaction and characterization of polymer. Results revealed that molecular weight, Tg, tensile strength, tear strength, hardness, contact angle and average particle size increase with increase of NCO/OH molar ratios. Elongation at break and viscosity decrease with increase of NCO/OH molar ratios. The increase of molecular weight, Tg, tensile strength, tear strength, hardness, contact angle and average particle size are attributable to the increase of free NCO content and hard segment in the prepolymer of high NCO/OH molar ratio.

**Key words:** Polyurethanes • Dispersions • Mechanical properties • Physical properties • NCO/OH molar ratio

### INTRODUCTION

Polyurethane dispersion (PUD) is a unique polymeric material with a wide range of physical and chemical properties and it has been used in various fields, such as foams, coatings, adhesives and thermoplastic elastomers [1-5]. An aqueous polyurethane dispersion is a binary colloidal system, where polyurethane particles are dispersed in a continuous aqueous medium. To be dispersible in water, polyurethane should contain ionic groups in its structure. <sup>6</sup> The incorporation of ionic groups into polyurethanes is a practical method to obtain aqueous polyurethane dispersions and various polyurethane ionomers have been described in the literature [7-14].

PUDs are segmented polymers comprising of soft segments joined by a hard segment urethane linkage. The soft segment is usually poly (glycol) and the hard segment consists of diisocyanate and chain extenders. The hard segments in PUDs affect particularly the modulus, hardness and tensile strength; whereas, soft segments primarily influence the elastic properties of

PUD [15]. The presence of an ionic group in the hard segment has a considerable effect on its physical properties and it is reasonable to suppose that the interaction between the acid groups and their counterions is responsible for these effects. The degree of neutralization [16-18], the type of counterion [19-20] and the amount of ionic compound [5, 23, 24] significantly influence the physical properties.

This article describes the preparation of (PUDs) from poly (oxytetramethylene) glycol (PTMG), poly(oxypropylene) poly(oxyethylene) triol (FA-703), dimethylol propionic acid (DMPA), isophorone diisocyanate (IPDI) and toluene diisocyanate (TDI). The influence of the different NCO/OH molar ratios on the physical and mechanical properties of emulsion-cast films was studied.

### MATERIALS AND METHODS

**Materials:** Poly (oxytetramethylene) glycol (PTMG,  $M_w = 2000$ , OH number = 55 mg/g, Korea PTG, Korea), poly (oxypropylene) poly (oxyethylene) triol (FA-703,

Table 1: Feed compositions of PUD synthesized with variable contents of polyol and isocyanate

	M1		M2		M3	
	-----		-----		-----	
	----- Polyols, OH -----					
Samples	Wt (g)	Wt (%)	Wt (g)	Wt (%)	Wt (g)	Wt (%)
PTMG	126.222	25.12	114.538	22.79	104.268	20.75
FA-703	6.246	1.24	11.698	2.33	16.499	3.28
DMPA	6.623	1.32	6.312	1.26	6.038	1.2
Mole of OH (gm/mole)	----- 0.1144 -----		----- 0.1080 -----		----- 0.1023 -----	
	----- Isocyanates, OCN -----					
TDI	3.588	0.71	5.642	1.12	8.018	1.6
IPDI	25.948	5.16	28.804	5.73	30.702	6.11
Mole of NCO (gm/mole)	----- 0.1373 -----		----- 0.1620 -----		----- 0.1842 -----	
	----- NCO/OH -----					
Molar ratio	----- 1.20 -----		----- 1.5 -----		----- 1.8 -----	
NMP	13.247	2.64	12.624	2.51	12.077	2.40
TEA	4.997	0.99	4.762	0.95	4.555	0.91
EDA	1.376	0.27	3.245	0.65	4.919	0.98
Water	314.253	62.54	314.875	62.66	315.424	62.77

$M_w$  = 3200, OH number = 33 mg/g, Korea Polyols, Korea) were dried and degassed at 80°C, 1 - 2 mm Hg for 2 h before use. Dimethylol propionic acid (DMPA,  $M_w$  = 134.13, Aldrich) was dried at 50°C for 48 h, while isophorone diisocyanate (IPDI,  $M_w$  = 222.29, Bayer) and toluene diisocyanate (TDI,  $M_w$  = 174.16, Merck) were used as received. Triethylamine (TEA,  $M_w$  = 101.19, Merck) was dried over molecular sieves (Å), ethylenediamine (EDA,  $M_w$  = 60.1, Merck), N-methyl-2-pyrrolidinone (NMP, Fluka) and deionized (DI) water was used throughout the reaction.

**Preparation of Pre-Polymer:** The PUDs were prepared as previously described in the literature [7-14]. Polymerization was performed in a 500 mL round-bottom, four-necked separable flask with a mechanical stirrer, thermometer and condenser with drying tube. The reaction was carried out in an  $N_2$  atmosphere in a constant-temperature oil bath. IPDI, TDI and polyol were charged into the reactor and the mixture was heated at 100°C for 1 h. After that, DMPA and NMP were added to the mixture and the reaction proceeded at the same temperature until the theoretical NCO value was reached, as determined by the di-n-butylamine titration method [25, 26]. Samples were prepared by different NCO/OH molar ratios which are shown in Table 1.

**Neutralization and Dispersion of the Prepolymer:** After the prepolymer temperature dropped to 40°C, the carboxylic acid groups were neutralized by the addition of triethylamine (TEA) and the degree of neutralization is

100%. The mixture was stirred for further 20 min to ensure the reaction was completed. Then, the prepolymers were dispersed by adding distilled water to the prepolymer solution which was stirred vigorously. The addition rate was controlled carefully using a tubing pump with a calibrated flow rate [27]. Finally 10 wt% ethylenediamine aqueous solution was added to extend the chain at room temperature. The emulsion was stable for more than 6 months after preparation at room temperature.

**Film Preparation:** Films were prepared by casting the aqueous dispersions on surfaces and allowing them to dry at room temperature for 7 days and then at 60°C, for 12 hours [28-29]. The films were stored in a desiccator at room temperature for further characterization and measurements.

**Measurements:** Particle size and distribution were measured by laser light scattering (Sema Tech, SEM-633, He-Ne laser). The samples were diluted to the required concentration with distilled water before the measurement. FTIR spectra were recorded on a Bruker Tensor 37 FTIR spectrometer. The viscosity ( $\eta$ ) of the dispersions were measured using a Brookfield viscometer (Model LVTDV-II) at a shear rate of 100  $S^{-1}$  at 25°C. The contact angle formed between the water drops and the surface of the sample was measured using contact angle measuring system CAHN DCA-322 analyzer operated at 25°C with water drop and a velocity of 100  $\mu m/s$ . The drop of water was mounted on the surface to be tested with a micro-syringe and contact angle was measured from the view of

water drops as observed on monitor. Results are the mean value of three measurements on different parts of the film. The tensile properties of the emulsion cast films were measured by using MTS 10/M tensile testing machine at a crosshead speed of 50 mm/min. An average of at least 4 measurements was taken and the 1-kN load cell was used. Shore A hardness was measured using an indentation hardness tester according to ASTM D2240-75. Glass transition temperature of samples were measured using differential scanning calorimetry (DSC), on a NETZSCH DSC200 PC, using aluminum crimped pans under  $N_2$  flow at  $20 \text{ mL min}^{-1}$ . The measurements were carried out between  $-100^\circ\text{C}$  and  $+100^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ . Molecular weights of the PUD were obtained from gel permeation chromatography (Waters Co., USA) equipped with a series of  $\mu$  Styragel® columns ( $10^4$ ,  $10^5$ ,  $10^6$  Å pore sizes), HPLC pump (Waters 501), RI detector (Waters 410) and integrator at  $40^\circ\text{C}$ . Polystyrene standards and universal calibration were adapted to reduce measuring error. Sampling of the PUD was carried out five times during the chain extension step to investigate the effects of molecular weights. Tetrahydrofuran (THF) was used as an eluent at  $1.0 \text{ mL min}^{-1}$  flow rate and  $1.0 \times 10^3 \text{ Pa}$  pump pressure.

## RESULTS AND DISCUSSION

**FT-IR Analysis:** IR spectrum obtained from the cast film is shown in Figure 1. This analysis was used to check the end of polymerization reaction, verifying the disappearance of the  $\nu$  NCO at  $2260 \text{ cm}^{-1}$  and the appearance of  $\nu$  N - H at  $3295 \text{ cm}^{-1}$ . The presence of expected peaks implies that the reaction was completed and the predesigned PUD was formed. IR spectra also contains all the related information on the primarily structure of the final polymer. An absorption band of the N - H stretching mode at  $3295 \text{ cm}^{-1}$  was observed. Aliphatic C - H stretching mode of  $2785\text{-}2940 \text{ cm}^{-1}$  and carbonyl (C = O) stretching absorption band at  $1735 \text{ cm}^{-1}$  were observed. N - H bending vibrations at  $1553 \text{ cm}^{-1}$ , C - O - C stretching absorption bands corresponding to the ether oxygen of the soft-segment at  $1005\text{-}1152 \text{ cm}^{-1}$  were also observed. These vibrations are strong evidence for the formation of PUD. The N - H group in polyurethane could form hard segment H - bonding with the carbonyl oxygen and soft H - bonding with the ether oxygen. The stronger hard-hard segment H - bonding acts as physical cross-links leading to difficult segmental motion of the polymer chain which results in a more significant phase separation between the hard and soft segments. The phase separation improves

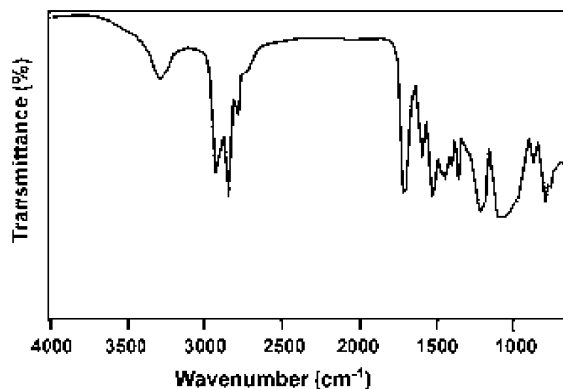


Fig. 1: IR spectrum of PUD

the mechanical properties of polyurethanes but reduces the flexibility and solubility [30, 31].

**Physical Properties:** The physical properties of the PUD films depend on the molecular structure, the content of functional groups and the molar ratio of NCO/OH. In PUDs, particle size and viscosity are important parameters. For example, dispersions with relatively large average particle size are generally unstable with respect to sedimentation. Dispersions with smaller particle size are more useful since such dispersions have high surface energy which enhances film formation.

The effect of NCO/OH molar ratios on average particle size diameter and viscosity of PUDs is shown in Table 2. The average particle size of PUDs depends on several factors such as stirring speed, prepolymer viscosity and the rate of water addition, but it is mostly governed by concentration of hydrophilic groups, i.e., carboxylic acid [32, 33]. The average particle size increased and the viscosity of PUDs decreased as NCO/OH molar ratio increased. The average particle size of the PUDs increased as the hydrophilicity of prepolymer decreased. With increasing NCO/OH molar ratio, the number of ionic groups in PUDs decreased [33].

It is known that the ionic groups are located predominantly on the surface of particles and the ionomer dispersions are stabilized by the formation of electrical double layers. With an increase in the size of the polymer dispersion particles, the relative size of the water layer to total particle size is decreased. With increase in particle size, the number of dispersed particles and viscosity decrease. Hence, the effective hydrodynamic volume of the dispersed phase decreases and the force of friction among particles decrease, resulting in a decrease in viscosity (Table 2). The results also reveal that particle size and viscosity are directly related to the NCO/OH molar ratios.

Table 2: Physical properties of the PUD emulsion cast films

Samples	M1	M2	M3
Particle size (nm)	40.20	70.50	95.70
Viscosity (cps)	172.50	75.80	55.40
Contact angle (deg)	89.00	90.00	92.00
Tg (°C)	-53.89	-47.01	-30.59

The hydrophilicity of the PUDs with different NCO/OH molar ratios were evaluated by measuring the contact angle between the water drops and the surface of the PUD using contact angle measuring system CAHN DCA-322. Table 2 shows the contact angle of the dispersion cast film with water drops. As seen in Table 2, a remarkable difference in contact angle between the PUDs samples with different NCO/OH molar ratio had been observed. Contact angle increases from (89) for M1 to (92) for M2. Thus, as expected, hydrophilicity decreased with increased NCO/OH molar ratio and, hence, the swell in water decreased and the contact angle with the water increased.

**Mechanical Properties:** The NCO/OH molar ratio is important for the properties of PUDs. As shown in Figure 2, tensile strength increased and elongation at break decreased as the NCO/OH molar ratios increases. This may be due to the increase in hard segments and hydrogen-bonding interactions between the chains in the PUDs [16, 29, 34]. It is known that the structure and reactivity of isocyanates can affect the tensile properties. [35]. A similar behavior was reported by other researchers. [36]. Also, it can be observed that the increase in NCO/OH molar ratio improved the tear strength and hardness of the PUDs

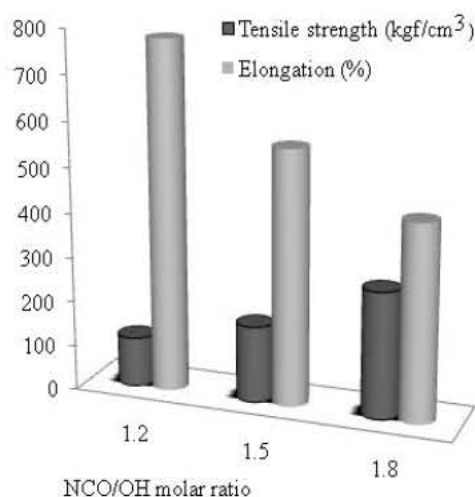


Fig. 2: The effect of NCO/OH molar ratio on tensile strength and elongation of PUD

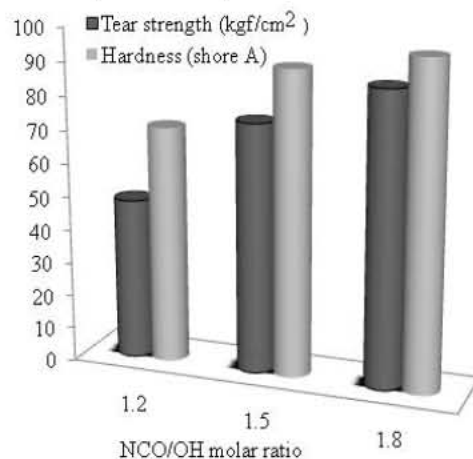


Fig. 3: The effect of NCO/OH molar ratio on tear strength and hardness of PUD

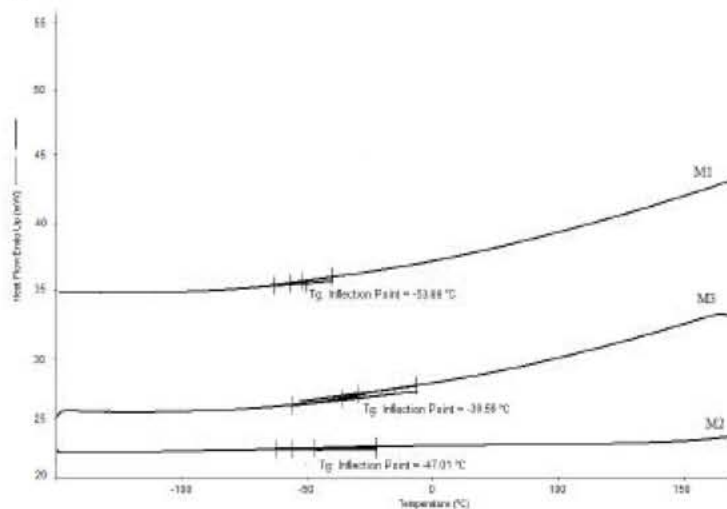


Fig. 4: DSC curves of PUD

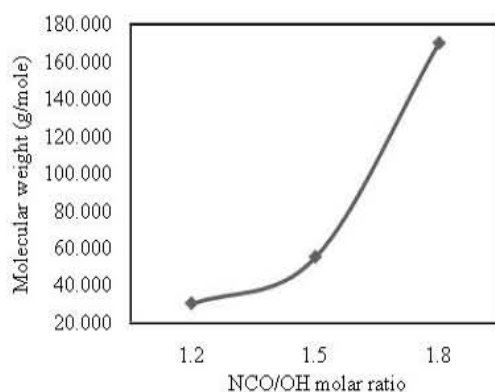


Fig. 5: Molecular weights of PUD as a function of NCO/OH molar ratios

(Figure 3), because of increasing in the degree of inter-chain hydrogen bonding, which leads to the formation of more rigid film.

The influence of the NCO/OH ratio on the thermal properties of the PUDs was also studied by DSC. The DSC thermograms corresponding to the first run of the PUD films with different NCO/OH ratio are shown in Figure 4. All of the films show only one glass transition temperature ( $T_g$ ), which increases from - 53.89°C to - 30.59°C with an increase in the NCO/ OH ratio of the PUDs. This might be due to more urea groups which were formed at higher NCO/OH molar ratio and the increased content of the hard segments that provide stronger physical crosslinking through hydrogen bonding [37, 38]. During the DSC heating run, no melting or crystallization transition is observed, indicating that the crystallization kinetics was very slow.

The weight average molecular weights ( $M_w$ ) of the PUDs with different NCO/OH molar ratio are given in Figure 5. The molecular weights of PUD increase with increasing NCO/OH molar ratio of PUDs. Increasing the NCO/OH molar ratio enriched residual NCO groups that react with ethylenediamine (chain extension). In addition, the chain extension produced urea linkages that contribute to hard segments of PUD. Therefore, mechanical property increased with the increase of the hard segment and molecular weight [39, 40].

### CONCLUSION

A series of PUDs were synthesized from TDI, IPDI, PTMG and FA-703 with different NCO/OH molar ratios according to the prepolymer mixing process.

Average particle size of the prepared PUD emulsions increases and the viscosity decreases with the increasing NCO/OH molar ratio. Molecular weight,  $T_g$ , tensile strength, tear strength, hardness and contact angle increase with the increasing of NCO/OH molar ratio. The increase in tensile properties and molecular weight is interpreted in terms of increasing hard segments in the prepolymer of high NCO/OH molar ratio.

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