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## Development of polyurethane dispersion based on aromatic isocyanat: influence of NCO/OH ratio on physico-mechanical properties of PUD

**Abstract:** Aqueous polyurethane dispersions (PUDs) were prepared by the prepolymer mixing technique solvent-free using aromatic isocyanat[*toluene diisocyanate (TDI)*], poly(oxytetramethylene) glycol (PTMG), dimethylol propionic acid (DMPA). The properties of both the dispersion's and casting polymer films were characterized by particle size analyzer, viscosity and tensile tester. IR spectroscopy was used to check the end of polymerization reaction and characterization of polymer. The effect of NCO/OH molar ratio on the physico-mechanical properties of the polyurethanes was studied. Results showed that tensile strength, 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.

**Key words:** polyurethanes; NCO/OH ratio; mechanical properties; physical properties; TDI

### Introduction

Polyurethanes dispersions (PUDs) are a two-phase system comprised of polyurethane polymer particles suspended in an aqueous continue phase [1-3]. PUDs have been synthesized by a number of different process including, the acetone process, the melt dispersion process, and the prepolymer mixing process [4]. In the acetone process, urethane prepolymer is dissolved in an organic solvent, as acetone or methylethylketone. After polyaddition, water is added to the mixture until the system spontaneously under goes a phase inversion[5]. The acetone process yields is a high quality reproducible product, but the disadvantages of this process are organic solvents that required in the original polymer formation. In the melt dispersion process, the chain extension is initiated either before or during the dispersion with water, but the disadvantage of this process is the high viscosity in the final products that need heating eliminates or large amounts of organic solvent to reduce the viscosity [5-7]. In the prepolymer mixing process, surfactants are added before dispersion with water. Surfactant is a surface-active agent that containing carboxyl group typically dimethylolpropionic acid (DMPA). Advantages of this process is that polymer synthesis is carried out in the aqueous two phases system with little or no addition of organic solvent and ability to control the strength of

cross-linking in the final polymer particle[8]. A number of researcher developed PUDs by different technique including, polyols, isosyanat, chain extension, neutralization step and NCO/OH ratio [9-14]. The NCO/OH molar ratio determines the molecular weight of the prepolymer in the first stage of the synthesis and consequently the relative proportion of the urethane and urea groups in the final polymer chain. As an ultimate result, this ratio will therefore affect both the properties of the dispersions, such as particle size, and the dry polymer thermal and mechanical properties [13]. As expected, and in agreement with previously reported results by other authors [15], physico-mechanical properties of polyurethane dispersion based on TDI and IDI increases with increasing NCO/OH ratio [2]. In particular, it showed that aliphatic diisocyanates like TMXDI and IPDI are much more appropriate than aromatic structures or symmetric aliphatic ones and that the [NCO]/[OH] ratio plays a fundamental role and gives the most promising products in terms of small particle size in the dispersions and physical properties of the final polymer films, when it approaches a value of 2 [13]. Negim et al [16] studied the effect of NCO/OH molar ratio on the physico-mechanical properties of the polyurethanes. Polyurethane dispersion were based on isophorone diisocyanate (IPDI), toluene diisocyanate (TDI), poly(oxytetramethylene) glycol (PTMG), dimethylol propionic acid (DMPA)

and poly(oxypropylene) poly(oxyethylene) triol (FA-703). Results revealed that molecular weight, T<sub>g</sub>, 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, T<sub>g</sub>, 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.

The present article deals with a series of PUD formulations, used with variable NCO/OH ratios and involving aromatic diisocyanates (TDI), poly(oxytetramethylene) glycol (PTMG), dimethylol propionic acid (DMPA). The characterization of the aqueous dispersions and cast films were studied.

## Materials and methods

### Materials

Poly(oxytetramethylene) glycol (PTMG, M<sub>w</sub> = 2000, OH number = 55 mg/g, Korea PTG, Korea) was dried and degassed at 80 °C, 1 – 2 mm Hg for 2 h before use. Dimethylol propionic acid (DMPA, M<sub>w</sub> = 134.13, Aldrich) was dried at 50 °C for 48 h, while toluene diisocyanate (TDI, M<sub>w</sub> = 174.16, Merck) was used as received. Triethylamine (TEA, M<sub>w</sub> = 101.19, Merck) was dried over molecular sieves (Å), ethylenediamine (EDA, M<sub>w</sub> = 60.1, Merck), N-methyl-2-pyrrolidinone (NMP, Fluka) and deionized (DI) water was used throughout the reaction.

### Preparation of prepolymer

The PUDs were prepared as previously described in the literature [17-22]. 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<sub>2</sub> atmosphere in a constant-temperature oil bath. 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 [19, 20]. The reaction scheme for the prepolymer preparation and the processes of dispersion and chain extension are shown in scheme 1. Samples were prepared by different NCO/OH molar ratios are shown in Table 1.

**Table 1** – Feed compositions of PUD synthesized with variable NCO/OH ratio

| Samples   | A1       | A2     | A3     |
|-----------|----------|--------|--------|
| Materials | Wt. (gm) |        |        |
| PTMG      | 140.00   | 140.00 | 140.00 |
| DMPA      | 7.00     | 7.00   | 7.00   |
| TDI       | 31.92    | 42.56  | 53.21  |
| TEA       | 5.28     | 5.28   | 5.28   |
| Water     | 351.30   | 378.95 | 404.47 |
| EDA       | 3.67     | 7.34   | 11.02  |
| NCO       | 0.1833   | 0.2444 | 0.3055 |
| OH        | 0.1222   | 0.1222 | 0.1222 |
| NCO/OH    | 1.50     | 2.00   | 2.50   |

### Neutralization and dispersion of the prepolymer

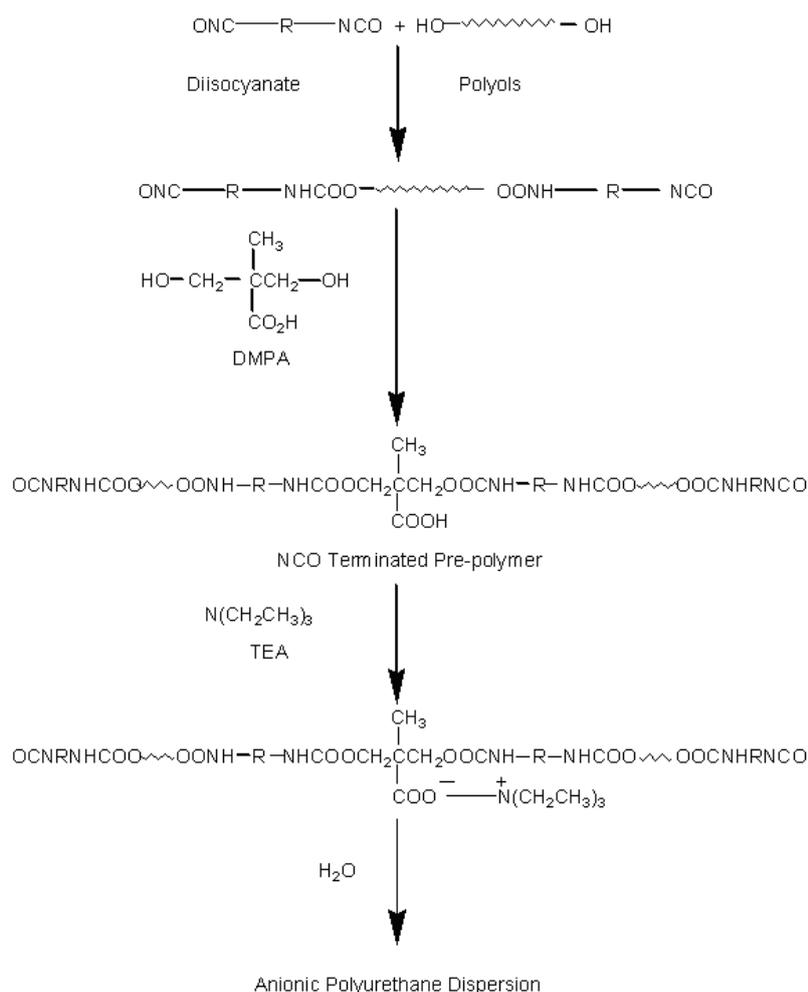
After the prepolymer temperature dropped to 40°C, the carboxylic acid groups were neutralized by the addition of triethylamine (TEA) and the degree of neutralization is 100%. The mixture was stirred for further 20 min to ensure the reaction was completed. Then, the prepolymers were dispersed by adding 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 [21]. 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 [22-23]. 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 was measured using a Brookfield viscometer (Model LVTDV-II) at a shear rate of 100 S<sup>-1</sup> at 25°C.



**Scheme 1** – Formation of PU dispersion having anionic centre.

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  $\mu\text{m/s}$ . 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.

## 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 NCO at  $2265\text{ cm}^{-1}$  and the appearance of N-H at  $3291\text{ cm}^{-1}$ . The presence of expected peaks implies that the reaction was completed and the pre-designed PU 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  $3291\text{ cm}^{-1}$  was observed. Aliphatic C-H stretching mode of  $2795\text{--}2938\text{ cm}^{-1}$  and carbonyl (C=O) stretching absorption band at  $1730\text{ cm}^{-1}$  were observed. N-H bending vibrations at  $1550\text{ cm}^{-1}$ , C-O-C stretching absorption band corresponding to the ether oxygen of the soft segment at  $1000\text{--}1150\text{ cm}^{-1}$  were also observed. The band at  $1507\text{ cm}^{-1}$  was also observed for aromatic ring stretch. These vibrations are strong evidence for the formation of PU. The N-H group in polyurethane could form hard segment H-bonding with the carbonyl oxygen and hard-soft H-bonding with the ether oxygen. The stronger hard-hard segment H-bonding acts as physical crosslinks

leading to difficult segmental motion of the polymer chain, which results in a more significant phase separation between the hard and soft segments.

#### *Physical and mechanical properties*

The effect of NCO/OH on the particle size and viscosity of PUD are shown in Figure 2. The result showed that particle size increased with increasing NCO/OH molar ratio. With increasing NCO/OH molar ratio, the number of ionic groups in PUDs decreased. However, the particle size of NCO/OH (1.5) has smaller particle size (35 nm), while NCO/OH (2.5) has larger particle size (76.5 nm) as shown in Figure 2. In general, the particle size is very important parameter in paint industrial; 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. Figure 2 shows the effect of NCO/OH molar ratio on the viscosity of PUD. It can be seen that the viscosity increased with decreasing NCO/OH molar ratio. The increase in viscosity of PUD due to the decreasing of particle size. It is important in paint application that the viscosity of the prepolymer, so NCO/OH (2.5) has standard viscosity (50 cps) for paint application. A suitable viscosity range is required to avoid sagging (in case of low viscosity) and practical difficulty in application (encountered with very high viscosity).

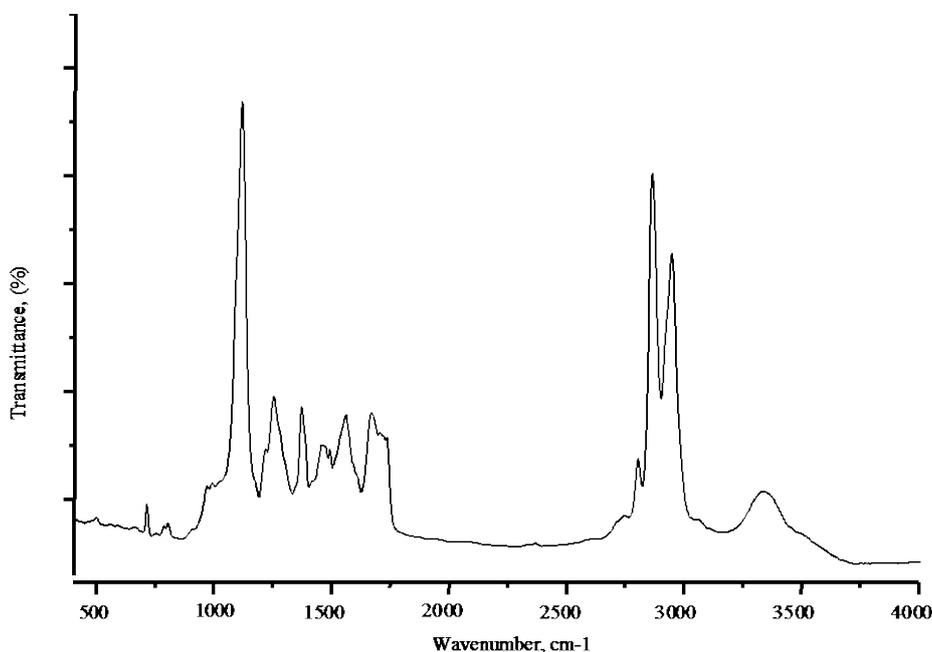


Figure 1 – FTIR of polyurethane dispersion.

Advancing and receding contact angle measurements of the films cast from PUDs could provide more information on the hydrophilicity of dried cast films. A better understanding of the hydrophobicity of the cast films could be obtained from dynamic contact angle studies rather than from swelling studies. The effect of NCO/OH molar ration on the contact angle of PUD films is shown in Figure 2. The results showed that contact angle decreased with increasing NCO/OH ratio. The results confirm that chain rigidity (NCO) is a more significant factor in controlling the contact angle, because chain rigidity does not allow the ionic groups to come near the particle surface

(22, 23). From the contact angle test, gave information about the best molar ratio (NCO/OH) for painting application because the increased contact angles using water means the films showed poorer wetting, adhesion, and application. Generally, if the water contact angle is smaller than  $90^\circ$ , the solid surface is considered hydrophilic and if the water contact angle is larger than  $90^\circ$ , the solid surface is considered hydrophobic. Contact angle test showed that PUD films with different NCO/OH films are hydrophilic.

The NCO/OH molar ratio is important for the properties of PUDs. As shown in Figure 3, 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 (NCO) and hydrogen-bonding interactions between the chains in the PUDs. However, the mechanical properties of PUD prepared in second report are higher than that of prepared in the first report. NCO/OH. Also, it can be observed that the increase in NCO/OH molar ratio improved the mechanical properties because of increasing in the degree of inter-chain hydrogen bonding, which leads to the formation of more rigid film. The high quality industrial polymer should behaving adhesive and film forming (24).

### Conclusions

A series of PUDs were synthesized from TDI, PTMG and DMPA 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. Tensile strength and contact angle increase with the increasing of NCO/OH molar ratio. The increase in tensile properties is interpreted in terms of increasing hard segments in the prepolymer of high NCO/OH molar ratio.

### Acknowledgements

The work was financially supported by Ministry of Science and Education of the Republic of Kazakhstan grant №0115PK00839

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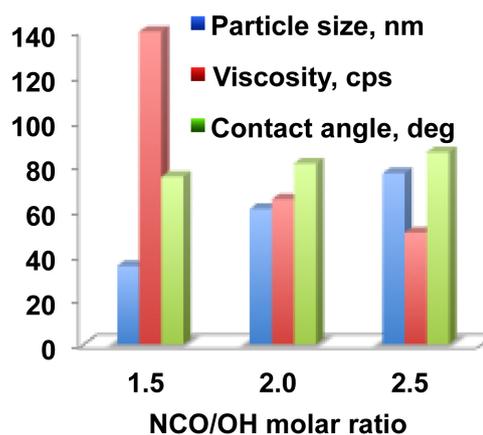


Figure 2 – The effect of NCO/OH ratio on particle size, viscosity and contact angle of PUD

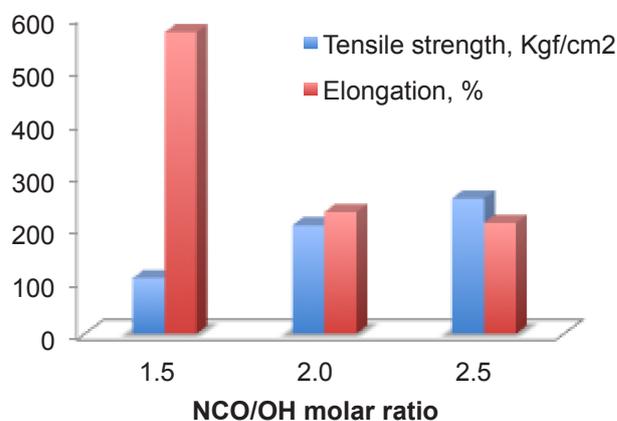


Figure 3 – The effect of NCO/OH molar ration on the tensile strength and elongation of PUD.

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