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## The effect of TDI, PTMG and DMPA on the physico-mechanical properties of polyurethane dispersion containing aromatic isocyanate

**Abstract:** The present paper relates to environment-friendly polyurethane dispersion having a high solids content of polyurethane polymer based on aromatic isocyanate. A series of water dispersion polyurethanes (PUDs) were prepared by polyaddition reaction using toluene diisocyanate (TDI), poly(oxytetramethylene) glycol (PTMG), and dimethylol propionic acid (DMPA). Physico-mechanical properties of PUDs were studied by average particle size, viscosity, contact angle, tensile strength and elongation. IR spectroscopy was used to check the end of polymerization reaction and characterization of polymer. Results revealed that tensile strength, tear strength, hardness, contact angle and viscosity increase with increase of the amount of TDI, PTMG and DMPA in the PUDs. Elongation at break and average particle size decrease with increase of TDI, PTMG and DMPA. The increase of physico-mechanical properties are attributable to the increase of free NCO content and hard segment in the prepolymer of high content of TDI, PTMG and DMPA.

**Key words:** polyurethanes; dispersions; mechanical properties; physical properties; TDI.

### Introduction

Polyurethane dispersions (PUDs) are well known and used in the production of different of useful polyurethane products, such as; adhesive, coatings, sealants, elastomers, fibers and foams [1-5]. PUDs are binary colloidal systems having polyurethane particle dispersed in aqueous phase together with an active hydrogen-containing chain extender, such as diamine [6]. Researchers are imperative develop PUD mainly due to the evolution of legislation towards reducing the VOC (volatile organic concentration) and the creation of environmentally friendly products. Wang et al [7] developed PUD by using trimethylolpropane, which was modified by 3-aminopropyltriethoxysilane to form highly crosslinked PUD. The results showed that, as the mass fraction of 3-aminopropyltriethoxysilane increases from 0% to 10%, water and ethanol absorption decreased. Vanesa et al [8] provided some useful indications on how to optimize the properties of polyurethane dispersions prepared by the prepolymer mixing technique without the use of any organic solvent. They used aliphatic and aromatic diisocyanates with the same polyols and chain extenders. In particular, it showed that aliphatic diisocyanates like [ $\alpha$ ,  $\alpha$ ,  $\alpha$ ']-tetramethyl-1,3-xylene

diisocyanate (TMXDI) and isophorone diisocyanate (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. Lee et al [9] modified polyurethane dispersion by enhancing the molecular weight in the preparation of the aqueous polyurethane dispersions derived from various polycarbonatediols, di(4-isocyanatocyclohexyl)methane (HMDI), and various carboxylic diols, including dimethylol propionic acid (DMPA), dimethylol butyric acid (DMBA), and a carboxylic polycaprolactonediol. The films of the polyurethane dispersions derived from the carboxylic polycaprolactonediol were significantly softer, and had lower tensile strength and moduli, and higher elongation than those derived from DMPA and DMBA. The dynamic mechanical property data indicate that the HMDI based polyurethanes dispersion films derived from DMBA and DMPA can exhibit higher temperature resistance than the isophorone diisocyanate (IPDI) based ones. Negim et al [10] studied the effect of NCO/OH ratio on the physico-mechanical properties of PUD. PUD 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). Results revealed that molecular weight,  $T_g$ , 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,  $T_g$ , 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 study deals with the preparation of PUDs from poly(oxytetramethylene) glycol (PTMG), dimethylol propionic acid (DMPA), isophorone diisocyanate (IPDI) The influence of variable TDI, PTMG and DMPA amounts 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)

was 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 toluene diisocyanate (TDI,  $M_w = 174.16$ , Merck) was used as received. Triethylamine (TEA,  $M_w = 101.19$ , Merck) was dried over molecular sieves ( $\text{\AA}$ ), 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 [11-18]. 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. 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]. Samples were prepared by different TDI, PTMG and DMPA, which are shown in Table 1.

**Table 1** – Feed compositions of PUD synthesized with variable contents of TDI, PTMG and DMPA.

Samples	A1	A2	A3
Materials	Wt., gm		
PTMG	361	237.3	159.6
TDI	62.87176	41.328168	27.795936
DMPA	10.7988063	7.2	4.8166083
TEA	8.1468069	5.431804927	3.6337329
Water	568.526	372.819	252.4
EDA	10.84805	7.130865	4.79598
OH	0.1805	0.11865	0.0798
NCO	0.361	0.2373	0.1596
NCO/OH	2	2	2

### 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 dis-

tilled 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-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  $\mu\text{m/s}$ . 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. Shore A hardness was mea-

sured using an indentation hardness tester according to ASTM D2240-75.

## Results and their 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 predesigned 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 2795–2938  $\text{cm}^{-1}$  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 1000–1150  $\text{cm}^{-1}$  were also observed. The bands 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.

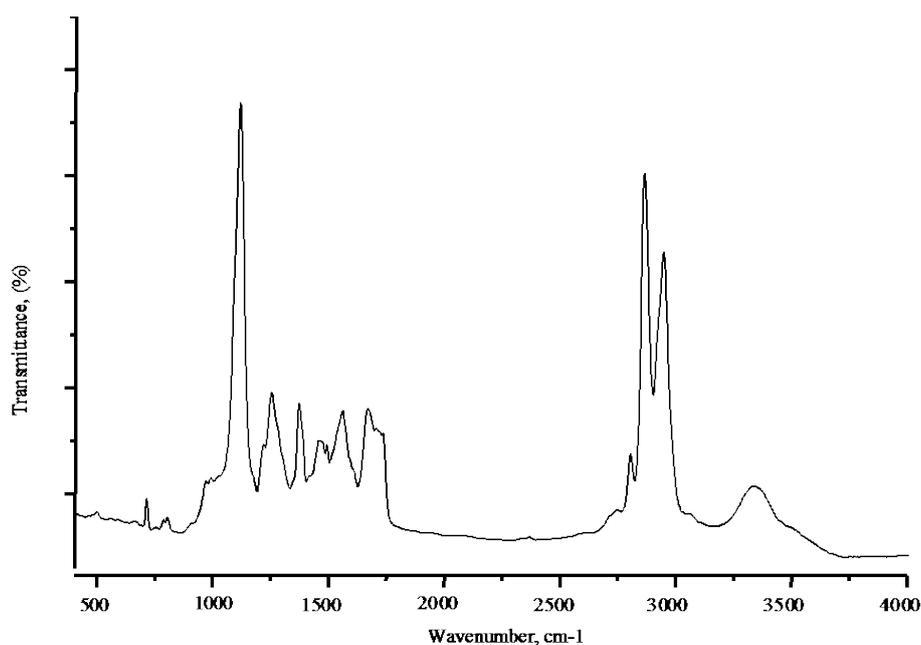


Figure 1 – FTIR of polyurethane dispersion.

*Physical properties:*

In PUD, the particle size could be controlled to some extent by emulsification conditions such as stirring speed or dispersing temperature which have an effect on the viscosity of prepolymer but it is mostly governed by the concentration of hydrophilic groups, i.e. carboxylic acids (24, 25). The particle size decreased as the DMPA content increased. The decreases of the particle size with increasing of DMPA content could be due to the stabilizing mechanism of the ionomer as shown in Table 2. However, particle size is important factor in PUD coatings. For example, in many surface coatings, relatively large particles are preferred to facilitate fast drying and relatively small particles are preferable when deep penetration of the dispersion into the substrate is an essential requirement.

**Table 2** – Physical Properties of the PUD Cast Films

Samples	A1	A2	A3
Particle size, nm	50.7	56.8	67.8
Viscosity, cps	60	38	25
Contact angle, deg	30	45	48

Table 2 shows the increasing in PUD viscosity with the increasing amount of PTMG, MPA and TDI, which also led to the increase in the total ionic content. The ionic content affects the dispersion viscosity in two ways. Due to the higher ionic content, the particle size of the dispersion decreases, and hence, dispersion viscosity increases due to the increase in the effective volume of the dispersed particle. When the ionic content is high, the repulsions between the ionic groups increases, leading to higher viscosity. The water contact angle decreased as the amount of PTMG, MPA and TDI were increased as shown in Table 2. The increased contact angles using water means the films showed poorer wetting with decreasing PTMG, MPA and TDI content.

*Mechanical properties:*

The mechanical properties of the PUD films with respect to the amount of PTMG, DMPA and TDI are shown in Table 3. It can be seen that tensile, tear strength and elongation increased with increasing amounts of PTMG, DMPA and TDI. The increase of tensile strength and tear strength are associated with increasing TDI, while increasing of elongation is associated with increasing PTMG and DMPA. Authors concluded that the hard segments act as crosslinks, inhibiting stress-relaxation and inducing stress-crys-

tallization of the soft segments that results in higher tensile strength [26, 27].

**Table 3** – Mechanical properties of the PUD Cast Films

Samples	A1	A2	A3
Tensile strength, Kgf/cm <sup>2</sup>	97.92	68.87	53.67
Tear strength, Kgf/cm <sup>2</sup>	24.196	21.92	15.7
Elongation, %	751.33	272.5	225.87
Hardness, shore A	95	82	73

It can be seen that hardness increased with increasing amounts of TDI, PTMG and DMPA in the prepolymer as shown in Table 3. A1 showed the largest hardness compared with A3 and A2. This is presumably due to the increased hard segment contents and hydrogen bonding density of the PUDs.

**Conclusion**

Aqueous polyurethane dispersions were synthesized with different content of TDI, PTMG, and DMPA. The effect of TDI, PTMG, and DMPA on the particle size distribution, contact angle, viscosity and mechanical properties are studied. Average particle size of the prepared polyurethane emulsions decreases, and the viscosity increases with the increasing amount of TDI, PTMG, and DMPA. Tensile strength, tear strength, elongation at break, and contact angle increase with the increasing of the amount of TDI, PTMG, and DMPA. The increase in tensile properties is interpreted in terms of increasing hard segments, chain flexibility and their phase separation in high content of TDI, PTMG, and DMPA -based polyurethane.

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