

# Effects of TDI and FA-703 on Physico-Mechanical Properties of Polyurethane Dispersion

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**ABSTRACT:** A series of water dispersion polyurethanes dispersions (PUDs) were prepared by polyaddition reaction using isophorone diisocyanate (IPDI), toluene diisocyanate (TDI), poly(oxytetramethylene) glycol (PTMG), dimethylol propionic acid (DMPA), and triol (trade name FA-703). Various formulations were designed to investigate the effects of process variables such as TDI and FA-703 on the physico-mechanical properties of PUD. IR spectroscopy was used to check the end of polymerization reaction and characterization of polymer. Evolution of the particle size distribution, contact angle,  $T_g$ , molecular weight, viscosity, and mechanical properties of the emulsion-cast films were significantly affected by variable content of TDI and FA-703. Average

particle size of the prepared polyurethane emulsions and contact angle decrease with increase of content of FA-703 and TDI. Molecular weight,  $T_g$ , tensile strength, tear strength, hardness, viscosity and elongation at break increase with increase of content of FA-703 and TDI. The increase of molecular weight, tensile strength, tear strength and elongation at break properties are interpreted in terms of increasing hard segments, chain flexibility, and phase separation in high content of FA-703 and TDI-based polyurethane. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 8–13, 2011

**Key words:** polyurethanes; dispersions; mechanical properties; physical properties; ionomers

## INTRODUCTION

Solvent-based polyurethanes (PUs) have been replaced by aqueous polyurethane dispersions (PUDs) due to demands of environmental regulations against volatile organic chemicals, and they have gained speedy development in coating, adhesive, textile sizing, etc.<sup>1,2</sup>

PUDs comprise polyurethane polymers or polyurethane-polyurea polymers that contain both urethane and urea groups and are obtained by polyaddition reactions of polyols, polyisocyanates, and polyamines.<sup>3</sup> The preparation of polyurethane dispersions by the prepolymer mixing process has received some attention in the literature.<sup>4–14</sup> In this process, a medium molecular weight polymer (the prepolymer) is synthesized by the reaction of suitable diols or polyols (usually polyether or polyester macrodiols) with a molar excess of diisocyanates or polyisocyanates. In this reaction mixture, an internal emulsifier is added to allow the dispersion of the polymer in water; this emulsifier is usually a diol with ionic groups (carboxylate, sul-

fonate, or quaternary ammonium salt) or nonionic groups [poly(ethylene oxide)]. The internal emulsifier becomes part of the main chain of the polymer. Approximately, 15% organic solvent, typically *N*-methyl pyrrolidinone (NMP), is used to reduce the viscosity of the medium as well as to dissolve the internal surfactant. The final step is the dispersion of the prepolymer in water followed by chain extension with a water soluble diamine to buildup the molecular weight of the polymer. It is generally accepted that the properties of polyurethanes (PU) ionomers are primarily due to the phase behaviour of soft and hard segments as well as their ionic character. Since ions are introduced into either hard or soft segments, and imparting many properties to the PU matrix, attention is being drawn to these PUDs ionomers.<sup>15–17</sup> The existence of the hard segment domains also gives PUDs ionomers excellent mechanical strength. The dispersion of polymers in water and properties of cast films are affected by the type and content of ionic centers and polyols as soft segment.<sup>18–25</sup>

This article describes the preparation of (PUDs) from poly(oxytetramethylene) glycol (PTMG), triol (FA-703), dimethylol propionic acid (DMPA), isophorone diisocyanate (IPDI), and toluene diisocyanate (TDI). The influence of the different contents of FA-703 and TDI on the physical and mechanical properties of emulsion-cast films, contact angle, viscosity, and particle size distribution was studied.

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## EXPERIMENTAL

### Materials

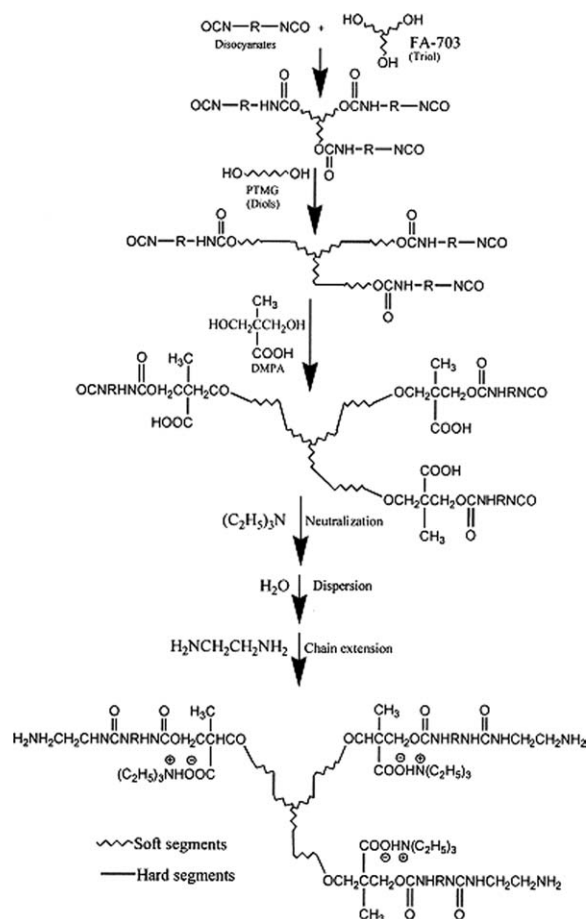
Poly(oxytetramethylene) glycol (PTMG,  $M_w = 2000$ , OH number = 55 mg/g, Korea PTG, Korea), triol trade name (FA-703,  $M_w = 3200$ , OH number = 33 mg/g, Korea Polyols, Korea) were dried and degassed at 80°C, 1–2 mm Hg for 2 h before use. Dimethylol propionic acid (DMPA,  $M_w = 134.13$ , Aldrich) 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 (A), ethylenediamine (EDA,  $M_w = 60.1$ , Merck), *N*-methyl-2-pyrrolidone (NMP, Fluka) and deionized (DI) water was used throughout the reaction.

### Preparation of pre-polymer

The polyurethane dispersions were prepared as previously described in the literature.<sup>4–14</sup> Polymerization was performed in a 500 mL round-bottom, four-necked separable flask with a mechanical stirrer, thermometer, and condenser with drying tube. 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.<sup>26,27</sup> 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 content of TDI and FA-703 with constant ionic content and chain extender which are shown in Table I.

### Neutralization and dispersion of the prepolymer

After the prepolymer temperature dropped to 40°C, the carboxylic acid groups were neutralized by the addition of 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.<sup>28</sup> 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.



Scheme 1 Formation of PUD having anionic center.

### Film preparation

Films were prepared by casting the aqueous dispersions on leveled surfaces and allowing them to dry at room temperature for 7 days, and then at 60°C, for 12 h.<sup>29–31</sup> 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 microsyringe, and contact angle was measured from the view of water drops as observed on monitor. Results are the mean value of

**TABLE I**  
**Feed Compositions of dispersion Polyurethanes Synthesized with Variable Contents of Polyol and Isocyanate**

Samples	M1		M2		M3	
	Wt (g)	Wt (%)	Wt (g)	Wt (%)	Wt (g)	Wt (%)
Polyols, OH						
PTMG	102.198	89.7	100.678	87.7	99.427	85.7
FA-703	2.2775	2.0	4.5896	4.0	6.958	6.0
DMPA	9.403	8.3	9.474	8.3	9.575	8.3
Total	113.879	100	114.742	100	115.960	100
Mole of OH (gm/mole)	0.1219		0.1224		0.1232	
Isocyanates, NCO						
TDI	2.4088	5	7.086	15	12.9726	30
IPDI	45.767	95	40.156	85	30.2694	70
Total	48.176	100	47.242	100	43.242	100
Mole of NCO (gm/mole)	0.2197		0.2213		0.2217	
NCO/OH	1.8					
NMP	18.806		18.948		19.149	
TEA	7.094		7.147		7.223	
EDA	5.852		5.867		5.91	
Water	306.193		306.054		305.851	

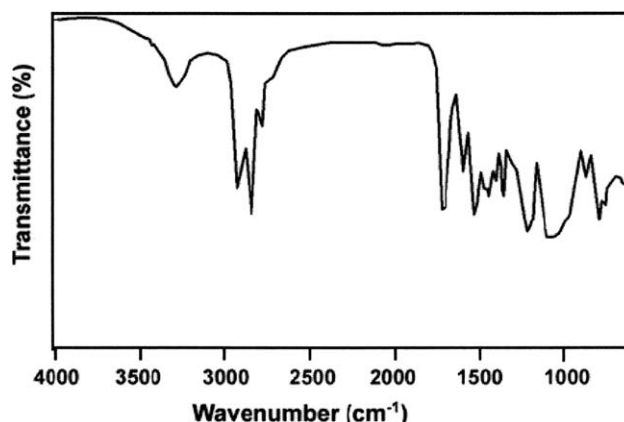
three measurements on different parts of the film. The tensile properties of the emulsion cast films were measured by using MTS 10/M tensile testing machine at a crosshead speed of 50 mm/min. An average of at least four measurements was taken, and the 1-kN load cell was used. Shore A hardness was measured 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<sub>2</sub> flow at 20 mL min<sup>-1</sup>. The measurements were carried out between -100°C and +100°C at a heating rate of 10°C min<sup>-1</sup>. Molecular weights of the PUD were obtained from gel permeation chromatography (Waters Co., USA) equipped with a series of  $\mu$  Styragel® columns (10<sup>4</sup>, 10<sup>5</sup>, 10<sup>6</sup> Å pore sizes), HPLC pump (Waters 501), RI detector (Waters 410), and integrator at 40°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 was used as an eluent at 1.0 mL min<sup>-1</sup> flow rate and 1.0 × 10<sup>3</sup> Pa pump pressure.

## RESULTS AND DISCUSSION

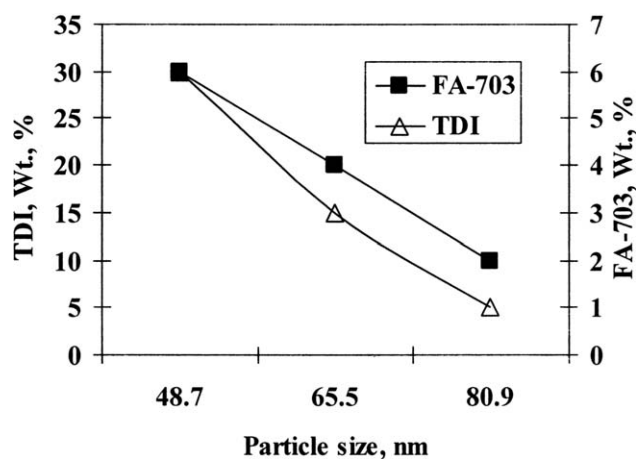
### FTIR analysis

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 2265 cm<sup>-1</sup> and the appearance of  $\nu$  N—H at 3291 cm<sup>-1</sup>. 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 cm<sup>-1</sup> was observed. Aliphatic C—H stretching mode of 2795–2938 cm<sup>-1</sup> and carbonyl (C=O) stretching absorption band at 1730 cm<sup>-1</sup> were observed. N—H bending vibrations at 1550 cm<sup>-1</sup>, C—O—C stretching absorption band corresponding to the ether oxygen of the soft segment at 1000–1150 cm<sup>-1</sup> were also observed. 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. The phase



**Figure 1** IR spectrum of polyurethane dispersion.



**Figure 2** Particle size of PUD as a function of FA-703 and TDI.

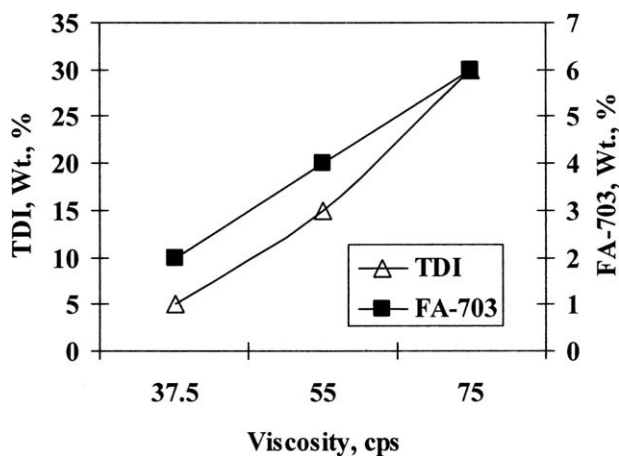
separation improves the mechanical properties of polyurethanes but reduces the flexibility and solubility.<sup>32,33</sup>

### Physical properties

The solid content of the dispersions was adjusted to 32% and all measurements were based on 32% solids content. The carboxylic groups of DMPA were completely neutralized by TEA in all the experiments.

Aqueous PUDs are mainly used in coatings. In PUDs, particle size and viscosity are important parameters. 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. A suitable viscosity range is required to avoid sagging (in case of low viscosity) and practical difficulty in application (encountered with high viscosity).

The variation of the average particle size of PUD having the same NCO/OH ratio with different amounts of FA-703 and TDI are shown in Figure 2. It can be seen that the particle size decreases with increasing amount of FA-703 and TDI. This decrease may be due to the intimate phase mixing of polyol compared with phase separation produced by the increasing amount of polyol, thus makes it difficult for ionic centers to leave the surface of particles during emulsification. In PUD, particle size is governed by the hydrophilicity in addition to external factors, such as shear force and temperature.<sup>34</sup> With the increased in total hydrophilicity, smaller particles result.<sup>34</sup> The hydrophilicity of FA-703 increases with the increase of its amount. With reduced particle size, the number of dispersion particles increases and higher dispersion viscosity results. Figure 3 shows the increasing in emulsion viscosity with the increasing amount of FA-703 and TDI, which also

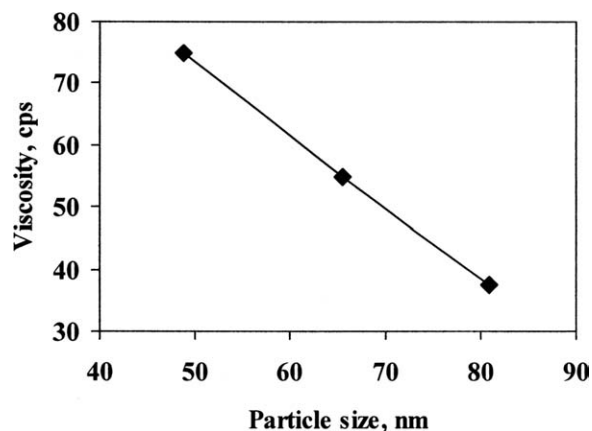


**Figure 3** Viscosity of PUD as a function of FA-703 and TDI.

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.

Particle size of the PUD depends on many factors, such as type of isocyanates, polyols, and viscosity of the prepolymer.<sup>35</sup> Figure 4 shows that the particle size decreases and the viscosity increases with increasing amount of FA-703 and TDI in the prepolymer. The increase in viscosity is mainly due to increase in chain flexibility of the polyurethane with the increasing amount of FA-703 and TDI. The results also reveal that particle size and viscosity are directly related to the amount of FA-703 and TDI.

Advancing and receding contact angle measurements of the films cast from PUD could provide more information on the hydrophilicity of dried emulsion-cast films. A better understanding of the hydrophobicity of the cast films could be obtained



**Figure 4** Particle size of PUD as a function of viscosity.

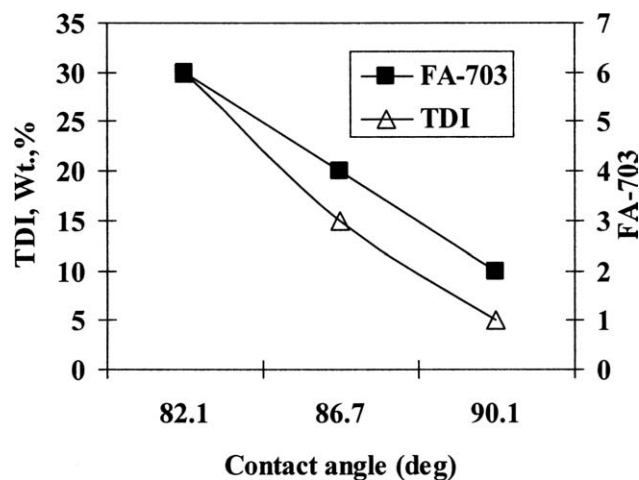


Figure 5 Contact angle of PUD as a function of FA-703 and TDI.

from dynamic contact angle studies rather than from swelling studies. Figure 5 shows the result of the dynamic contact angle study. The water contact angle decreased as the amount of FA-703 and TDI were increased. The increased contact angles using water means the films showed poorer wetting with decreasing FA-703 and TDI content. The hydrophilicity, chain flexibility, and phase separation increased with the increasing amount of FA-703 and TDI. The results confirm that chain flexibility 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.

### Mechanical properties

The mechanical properties of the PUD films with respect to the amount of FA-703 and TDI are shown in Table II. It can be seen that tensile and tear strength increased with increasing amounts of FA-703 and TDI in the prepolymer. M3 (FA-703, 6% & TDI, 30%) showed the largest tensile and tear strength compared with M2 (FA-703, 4% & TDI, 15%) and M1 (FA-703, 2% & TDI, 5%). This is presumably due to the increased hard segment contents and hydrogen bonding density of the PUDs. The elongation at break was increased with decreasing amount of FA-703 and TDI. It may be due to the increased in chain flexibility and phase separation of

TABLE II  
Mechanical Properties of the PU Emulsion Cast Films

Samples	M1	M2	M3
Tensile strength (kgf/cm <sup>2</sup> )	200.34	246.81	280.31
Elongation (%)	610.57	615.64	624.56
Tear strength (kgf/cm <sup>2</sup> )	86.89	87.23	88.24
Hardness (shore A)	75.5	89.9	95.1
T <sub>g</sub> , °C	-27.3	-24.6	-14.5

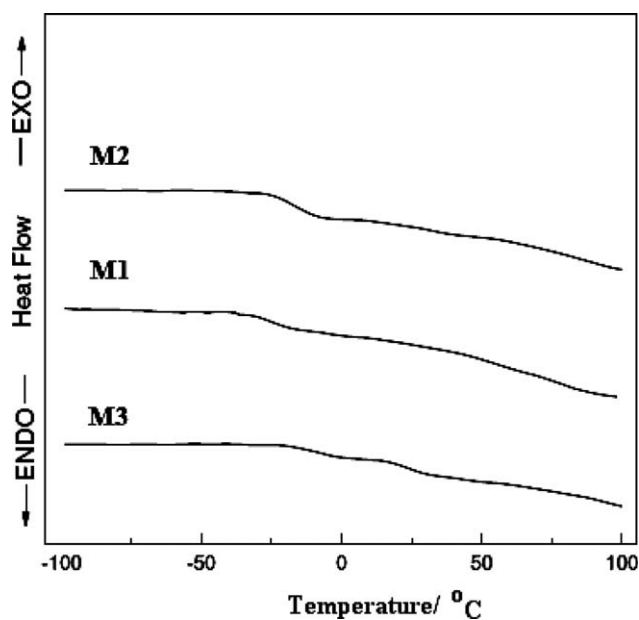


Figure 6 DSC curves of polyurethane dispersions.

the PUD. Similarly, hardness was found to increase with increasing of FA-703 and TDI.

The thermal transitions of polyurethane dispersions were determined by DSC analysis and are shown in Figure 6. The results of DSC analysis of PUD are summarized in Table II. Generally, it is known that  $T_g$  is directly proportional to crosslinking density and indirectly proportional to chain flexibility. Results are consistent with this statement. From Figure 6, it can be seen that the  $T_g$  of PUD moves toward the lower temperatures as the FA-703 & TDI decreases. The peak located at about  $-14.5^\circ\text{C}$  is shifted to about  $-27.3^\circ\text{C}$  as the FA-703 & TDI decreases from 6 to 2% and 30 to 5%, respectively. The decrease of  $T_g$  with decrease of FA-703 & TDI is

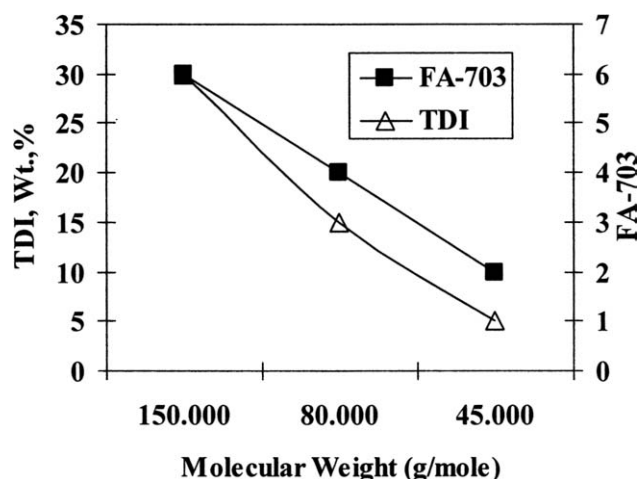


Figure 7 Molecular weights of polyurethane dispersion as a function of FA-703 and TDI.

mainly due to decreased hard segments and increased phase separation in the PU structure.

The weight average molecular weights ( $M_w$ ) of the PUD with different amounts of FA-703 and TDI are given in Figure 7. The  $M_w$  of PUD varied from 40,000 to 150,000 with increasing amount of FA-703 and TDI. Thus, as mentioned in the literature, an increase in the length of the flexible segment caused an increase in the molecular weight of prepolymer chains.<sup>36</sup>

### CONCLUSION

Aqueous polyurethane dispersions were synthesized from TDI, IPDI, PTMG, and FA-703 with different content of FA-703 and TDI. The effect of FA-703 and TDI 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 FA-703 and TDI. Molecular weight,  $T_g$ , tensile strength, tear strength, hardness, elongation at break, and contact angle increase with the increasing of the amount of FA-703 and TDI. The increase in tensile properties is interpreted in terms of increasing hard segments, chain flexibility and their phase separation in high content of FA-703 and TDI-based polyurethane.

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