Synthesis and Properties of Ionic Polyurethane Dispersions: Influence of Polyol Molecular Weight

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ABSTRACT

A series of water dispersible polyurethanes containing carboxylate anion as the hydrophilic pendant group were prepared from toluene disocyanate (TDI), 1,4-butanediol (1,4-BDO), dimethylol propionic acid (DMPA) and different molecular weight of polytetramethylene glycol (PTMG). IR Spectroscopy was used to check the end of polymerization reaction and characterization of polymer. The effect of PTMG molecular weight was studied on the particle size distribution, contact angle, and mechanical and thermal properties of the emulsion-cast films. Average particle size of prepared polyurethane emulsions decreases with increasing the PTMG molecular weight. Tensile strength and hardness decrease and elongation-at-break and contact angle increase with increase of the PTMG molecular weight. Thermal property and thermal stability are also affected by variation of PTMG molecular weight. The thermal stability increases with increasing PTMG molecular weight. Glass transition temperature \( T_g \) moved toward the lower temperatures by increasing molecular weight of the polyol. Decrease in \( T_g \) and tensile properties are interpreted in terms of the decrease in hard segments and the increase in chain flexibility and phase separation in high molecular weight PTMG based polyurethanes.

INTRODUCTION

Waterborne polyurethanes (PUs) have been gaining importance in a wide range of applications primarily, by environmental considerations of reducing solvent emissions into the atmosphere \([1,2]\). These polymers are very interesting industrial products. They have a broad spectrum of commercial uses in many market areas because of their wide range of chemical and physical properties they were obtained from different raw materials and synthetic processes \([3-5]\).

Aqueous PU dispersions can be

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classified into ionic and nonionic types. Nonionic types contain hydrophilic soft segment pendant groups such as polyethylene oxide [6], whereas the polymer chains of ionic types contain anionic or cationic centers. These centers could be pendant acid or tertiary nitrogen groups which are neutralized to form salts [7]. These groups are build up in the chain structure during the polymer preparation.

Several processes have been developed for the synthesis of PU dispersions [8-11]. All of these processes have common first step, in which a medium molecular weight prepolymer is formed by the reaction of suitable polyols with a molar excess of diisocyanates. 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 an ionic group (carboxylate, sulphonate, or quaternary ammonium salt) or a nonionic group (polyethylene oxide). The internal emulsifier becomes part of the main chain of the polymer. The critical step is the dispersion of the prepolymer in water and the molecular weight buildup in which the synthetic pathways differs in various processes. In this way, the most important processes are the acetone process, the prepolymer mixing process, the melt dispersion process, and the ketimine process [4]. In the melt dispersion process, the hydrophilically modified chain extended polymer is directly mixed with water.

It is now generally accepted that the properties of 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 being drawn to these PU ionomers [12-14]. The existence of the hard segment domains also gives PU ionomers an excellent mechanical strength. The dispersion of polymers in water and properties of cast films are affected by types and content of ionic centers and polyols as soft segment [15,16].

This article describes the preparations of ionic type waterborne PU from different molecular weight polytetramethylene glycol (PTMG), dimethylol propionic acid (DMPA), 1,4 butanediol (1,4-BDO) and, toluene diisocyanate (TDI). The influence of polyols molecular weight, were studied on the physical, mechanical and thermal properties of emulsion-cast films, contact angle, glass transition temperature, and particle size distribution.

**EXPERIMENTAL**

**Materials**

Polytetramethylene glycol (PTMG) with various molecular weights (Mn = 1000, 2000, and 3000) supplied by Arak Petrochemical Company) were dried and degassed at 80°C and 1-2 mmHg for 5 h before use. 1,4-Butanediol (1,4-BDO) (Merck) was dried and degassed at 50°C and 1-2 mmHg for 2 h. Dimethylol propionic acid (DMPA) (Aldrich) was dried at 100°C for 2 h in an oven. Dimethylformamide (DMF) (Merck), and triethylamine (TEA) (Merck) were dried over molecular sieves (4Å) and toluene diisocyanate (TDI) (Merck) was used as received.

**Preparation of Polymer**

A 250 mL round-bottom, four-necked flask with a mechanical stirrer, thermometer, condenser, nitrogen inlet, and pipette outlet was used as a reactor. The reaction was carried out in a constant temperature oil bath. PTMG was charged into the dried flask. When PTMG was stirring, the system was heated to 98°C, and then TDI was added slightly with dropper funnel. The mixture was heated at 98°C for 3 h to obtain NCO terminated prepolymer. After that, the solution of DMPA in DMF was added and stirring continued for 15 min and the system was cooled to 60°C. Butanediol was added at this temperature and after 15 min the neutralizing solution TEA dissolved in DMF charged into the reactor. The reaction scheme for the prepolymer preparation and the processes of dispersion and chain extension are shown in Scheme I. Samples were prepared by different molecular weights of polytetramethylene glycol (PTMG) with constant ionic content and chain extender which are shown in Table 1.

**Dispersion**

Aqueous dispersion of PU was obtained by adding deionized water (30°C) to the mixture (60°C). The rate of water addition is very important and is a critical parameter to obtain stable dispersion. Water should be added with a dropping funnel or dosing pump at a constant flow rate. The phase inversion was happened and the dispersion was obtained. The emulsion was stable over 5 months after preparation at room temperature.
Preparation of Films
Films were prepared by casting the aqueous dispersion onto a Teflon plate at room temperature, followed by drying at 40°C (1 day), 60°C (1 day), 70°C (1 day), and 85°C (1 day). 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 (SemaTech, SEM-633, He-Ne laser) at room temperature. The samples were first diluted in deionized water to 0.5% and the dispersions were homogenized.

The IR spectrum of the PU polymer films was

**Scheme I.** Formation of PU dispersion having anionic center.

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**Table 1.** Feed compositions of dispersion polyurethanes synthesized with various molecular weights of polyol.

<table>
<thead>
<tr>
<th>Samples</th>
<th>PTMG (Mn)  (g)</th>
<th>PTMG (g)</th>
<th>TDI (g)</th>
<th>DMPA (g)</th>
<th>1,4-BDO (g)</th>
<th>TEA (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM1</td>
<td>(1000)</td>
<td>12.5</td>
<td>6.6</td>
<td>2.5</td>
<td>0.56</td>
<td>1.8</td>
</tr>
<tr>
<td>SM2</td>
<td>(2000)</td>
<td>25</td>
<td>6.6</td>
<td>2.5</td>
<td>0.56</td>
<td>1.8</td>
</tr>
<tr>
<td>SM3</td>
<td>(3000)</td>
<td>37.5</td>
<td>6.6</td>
<td>2.5</td>
<td>0.56</td>
<td>1.8</td>
</tr>
</tbody>
</table>
obtained with a Fourier transform infrared (FTIR) spectrophotometer EQUINOX55-Bruker, equipped with HATR accessories and ZnSe crystal was used over the range 400-4000 cm\(^{-1}\) at room temperature.

Contact angle was measured by Gl0 (KRUSS) instrument through Sessile Drop method.

The thermogravimetric analysis (TGA) was carried out by using a thermogravimetric analyzer (Perkin Elmer pyris 1) at a heating rate of 10\(^{\circ}\)C/min in a nitrogen atmosphere from room temperature to 700\(^{\circ}\)C. The sample weights was 7-9 mg in all cases.

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 five measurements was taken and the 1-kN load cell was used.

Dynamic mechanical tests were performed with a PL-DMTA instrument (Polymer Laboratory) from -100 to 100\(^{\circ}\)C at a frequency of 1 Hz with a sample size of 1 3 cm.

RESULTS AND DISCUSSION

Preparation of aqueous PU dispersion was achieved via different molecular weight of polytetramethylene glycol (PTMG) and fixed dimethylol propionic acid (DMPA) content. The PU was prepared by reaction of stoichiometric amount of polyol/diisocyanate/chain extender with block ratios of 1:3:2 according to synthetic route as depicted in Scheme I. The polyol molecular weights (Mn) of 1000, 2000, and 3000 were used by controlling the NCO/OH ratio. DMPA, a carboxylic acid containing diol, have been used to form water-dispersible urethane prepolymer without any significant reaction between the carboxylic and isocyanate groups because the hydroxyl group is much more reactive than aliphatic isocyanate component.

IR Spectroscopy

IR Spectroscopy 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\(^{-1}\) and the appearance of \(\nu\) N-H at 3000-3400 cm\(^{-1}\). Presence of expected peaks implies that the reaction was completed and the predesigned PU was formed. IR Spectra also contains all the related information of the primarily structure of the final polymer.

An absorption band of the N-H stretching mode at 3291 cm\(^{-1}\) was observed. Aliphatic C-H stretching mode of 2795-2938 cm\(^{-1}\) and carbonyl (C=O) stretching absorption band at 1726 cm\(^{-1}\) were observed. N-H Bending vibrations at 1532 cm\(^{-1}\), C-O-C stretching absorption band corresponding to the ether oxygen of soft-segment at 1000-1150 cm\(^{-1}\) were also observed. These vibrations are strong evidence for the formation of PU.

The N-H group in polyurethane could form hard-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 cross-links leading to difficult segmental motion of the polymer chain which results in a more significant phase separation between hard and soft segments. The phase separation improves mechanical properties of polyurethanes but reduces the flexibility and solubility [17,18].

Effect of PTMG Molecular Weight

Particle Size

The effect of polyol molecular weight on particle size of the PU dispersions is shown in Figure 2. In these samples, the NCO/OH ratio was kept constant. It is seen that the particle size decreases from 94 to 50 nm with the increasing of molecular weight of polyol from 1000 to 3000. This decrease may be due to the intimate phase mixing of low molecular weight polyol compared with phase separation produced by of high molecular weight polyol. Decreasing molecular weight of the polyol makes it difficult for anionic centers to leave the surface of particles during emulsification.

Each particle in the dispersion is absorbed by a thin
layer of water due to the presence of hydrophilic -COOHN⁺(C₂H₅)₃ groups on the surface of the particles. With a decrease in the size of the polymer dispersion particles, the relative size of the water layer to total particle size was increased. With decrease in particle size, there is also an increase in the number of particles [19-21].

It is known that aqueous PU dispersions are two phase systems, in which water is the continuous phase. The dispersed phase is a solid polymer, although the aqueous PU dispersions obtained are seemingly clean solutions. It is well known that the particle size has a direct effect on the PU dispersion stability and that the larger average particle size (>1000 nm) is generally unstable with respect to sedimentation [17]. It is reasonably presumed that the anionic centers are hydrophilic in nature and predominantly located on the surfaces of PU particles in aqueous media. However with decrease in polyol molecular weight, deformation of hydrophobic-hydrophilic spherical structure in water is less possible and lead to a larger particle size at the stage of emulsification. The decrease of particle size with increasing molecular weight of PTMG has also related to the increased chain flexibility and larger soft segment-hard segment phase separation.

Contact Angle

The contact angle measurements of PU with different molecular weight of PTMG are shown in Figure 3. As it can be seen, there is a remarkable difference in contact angle between different molecular weights of PTMG, where it decreased from 90 for PTMG1000 to 81 for PTMG3000. This means that hydrophilicity, chain flexibility, and phase separation increased with increasing molecular weight of PTMG. The carboxylic ion of DMPA in the polymer is a hydrophilic group and serves as an internal emulsifier for polyurethane dispersions. However, 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 PUs with respect to PTMG molecular weight are shown in Table 3. It can be seen that tensile strength and hardness decreased with increasing PTMG molecular weight. SM1(PTMG 1000) showed the largest tensile strength compared with SM2 (PTMG2000) and SM3 (PTMG3000). It may be due to the higher hard segment contents for the same NCO/OH ratio and highest hydrogen bonding density. The elongation-at-break was increased with increasing molecular weights of PTMG. It may be due to increased chain flexibility and phase separation. Hardness decreased with increasing of PTMG molecular weight for the same reason (Table 3). The stress-strain curve of samples are also shown in Figure 4.

Table 2. The variation of particle size and contact angle with different molecular weights of PTMG in dispersion PU.

<table>
<thead>
<tr>
<th>Samples</th>
<th>PTMG (Mn)</th>
<th>Contact angle (deg)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM1</td>
<td>1000</td>
<td>90</td>
<td>94.4</td>
</tr>
<tr>
<td>SM2</td>
<td>2000</td>
<td>86</td>
<td>74.5</td>
</tr>
<tr>
<td>SM3</td>
<td>3000</td>
<td>81.2</td>
<td>50.2</td>
</tr>
</tbody>
</table>
TG Analysis

The TG curves of the samples as a function of PTMG molecular weights are shown in Figure 5. The initial decomposition temperature ($T_{d,\text{onset}}$), the temperature of half decomposition ($T_{d,\text{1/2}}$), and the temperature of the maximum rate of decomposition ($T_{d,\text{max}}$) for different samples at heating rate of 10$^\circ$C/min are listed in Table 4. The initial decomposition temperature ($T_{d,\text{onset}}$) is the temperature at which the loss of weight during heating is just measurable. The temperature of half decomposition ($T_{d,\text{1/2}}$) is the temperature at which the loss of weight during heating reaches 50% of its final value and the temperature of the maximum rate of decomposition ($T_{d,\text{max}}$) is the temperature at which the loss of weight reaches to its final value [22].

It can be seen that by increasing the molecular weight of PTMG, thermal stability of cast films increased. The degradation temperature of PU films based on PTMG 1000 is lower than PU films based on PTMG 2000 and PTMG 3000. It is said that the early stage degradation occurred mainly in the hard segments where urethane groups first undergo depolymerization, resulting individual monomers, then their further reaction produce carbon dioxide [21]. TGA studies of the PU films showed that the degradation of PU films starts at 210$^\circ$C and ended at 570$^\circ$C. The degradation at 570$^\circ$C corresponds to char formed.

DMTA Studies

Dynamic mechanical properties (storage modulus and tan $\delta$) of the emulsion cast films are shown in Figure 6. The glass transition temperature ($T_g$) of PU (tan $\delta$) moves toward the lower temperatures as the PTMG molecular weight increases. The tan $\delta$ peak located at

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**Table 3.** Mechanical properties of the PU emulsion cast films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile strength (MPa)</th>
<th>$T_g$ ($^\circ$C)</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM1</td>
<td>6.36</td>
<td>-1.28</td>
<td>91.4</td>
</tr>
<tr>
<td>SM2</td>
<td>3.74</td>
<td>-19.68</td>
<td>64.2</td>
</tr>
<tr>
<td>SM3</td>
<td>1.7</td>
<td>-25.21</td>
<td>61.4</td>
</tr>
</tbody>
</table>

**Table 4.** Thermal degradation behaviour of the PU films as a function of PTMG molecular weight (Mn).

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_{d,\text{onset}}$ ($^\circ$C)</th>
<th>$T_{d,\text{1/2}}$ ($^\circ$C)</th>
<th>$T_{d,\text{max}}$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM1</td>
<td>209.2</td>
<td>395.1</td>
<td>556.1</td>
</tr>
<tr>
<td>SM2</td>
<td>233.9</td>
<td>434.2</td>
<td>562.3</td>
</tr>
<tr>
<td>SM3</td>
<td>251.4</td>
<td>441.5</td>
<td>570.5</td>
</tr>
</tbody>
</table>

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**Figure 4.** Tensile properties of emulsion cast films as a function of PTMG molecular weight (Mn).

**Figure 5.** TGA Thermograms of PU emulsion’s cast films: (SM1) PTMG 1000, (SM2) PTMG 2000, and (SM3) PTMG 3000.

**Figure 6.** Dynamic mechanical properties (tan $\delta$) of emulsion cast films as a function of PTMG molecular weight (Mn).
about -1°C is shifted to about -25°C as the molecular weight of PTMG increases from 1000 to 3000. The decrease of \( T_g \) with increase of PTMG molecular weight is mainly due to increased chain flexibility and phase separation in PU structure.

**CONCLUSION**

Aqueous polyurethane dispersions were synthesized from TDI, PTMG, DMPA, and 1,4-BDO with different molecular weight of PTMG. The effect of PTMG on the particle size distribution, contact angle, mechanical and thermal properties are studied and concluded. Average particle size of prepared polyurethane emulsions decrease with increasing PTMG molecular weight. Tensile strength and hardness decrease and elongation-at-break and contact angle increase with increase of PTMG molecular weight. Thermal property and thermal stability is also affected by variation of TMDI molecular weight. The thermal stability increases with increasing PTMG molecular weight. Glass transition temperature (\( T_g \)) moved toward the lower temperature with increasing molecular weight of the polyl. The decrease in \( T_g \) and tensile properties is interpreted in terms of decreasing hard segments and increasing chain flexibility and phase separation in high molecular weight PTMG based polyurethanes.

**REFERENCES**

