Effect of NCO/OH Molar Ratio on the Structure and Properties of Aqueous Polyurethane from Modified Castor Oil

Li-Hong Bao¹, Yun-Jun Lan²*, and Shu-Fen Zhang¹

(1) State Key Laboratory of Fine Chemical, Dalian University of Technology, Dalian, Liaoning, 116012, P.R. China
(2) Zhejiang Key Laboratory of Leather Engineering, Wenzhou University, Wenzhou, Zhejiang, 325027, P.R. China

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A series of aqueous anionic polyurethane dispersions with ionic groups in the soft segments were synthesized from a polyether glycol, maleic anhydride modified castor oil, isophorone diisocyanate, and \( \alpha,\alpha \)-dimethylol propionic acid according to the prepolymer mixing process. Samples were neutralized by the addition of triethylamine. The reaction mixture was dispersed in water and the polymer chains were extended with ethylene diamine. The effect of NCO/OH molar ratio on the structure and properties of these polyurethanes were characterized by particle size analyzer, DSC, TG/DTG, IR, WAXD and tensile tester, etc. Particle size distribution becomes broader and the average particle diameter increases as NCO/OH molar ratio increases, which is mainly attributed to the decrease in chain flexibility and increase in viscosity of the dispersed particles. IR Study shows that the hydrogen bonding increases with increasing NCO/OH molar ratio. DSC Results identify that the phase mixing increases when some ionic groups were incorporated in soft segments and phase separation increases as NCO/OH molar ratio increases. TG/DTG Results show better thermostability under higher NCO/OH molar ratio that can be attributed to forming thermostable urea groups and more intermolecular hydrogen bonding. Broad scattering halos of WAXD graphs imply that all the samples are amorphous. The tensile strength and hardness of the polyurethane films increase with increasing NCO/OH molar ratio.

INTRODUCTION

As environmental protection and legislation requirements, waterborne polyurethane (PU) has substituted solvent-borne PU gradually in adhesive and coating industries in the past several decades [1,2]. In general, PU comprises linear copolymers with soft and hard segments structures. The soft segment is usually poly(glycol), and the hard segment consists of diisocyanate and chain extenders, e.g. diols and diamines. The hard segment provides physical cross-links through hydrogen bonding and filler-like reinforcement to the soft segment, which plays a key role in imparting the elasticity to PU mate-
The distributions and contents of hard and soft segments, and the NCO/OH molar ratio of prepolymer are main factors to affect the structure and organization of PU, and the sequential microphase separation and properties [4-6]. There has been a wide range of works in the synthesis and characterization of waterborne PU [7,8]. They are most often prepared by dispersing an isocyanate terminated PU prepolymer, which contains stabilizing groups, in water. Without high shear forces and external emulsifiers, excellent storage stability of the aqueous dispersion can be achieved if the number of stabilizing groups is sufficiently high. However, in previous instances the ionic groups were located in the hard segment. These ions increase the polarity of the hard segment and hence decrease the compatibility of the hard and soft segments. As a result, the phase separation was enhanced [9,10].

In this paper, we describe a new series of waterborne PU dispersions where the ionic groups are incorporated in both soft and hard segments using modified castor oil, polyether glycol (Ng210), and isophorone diisocyanate (IPDI) as main materials according to prepolymer mixing process. The effect of NCO/OH molar ratio on the dispersion characteristics and properties of dispersion casting films are studied.

EXPERIMENTAL

Materials
Castor oil (CO: hydroxyl value=163 mg KOH/g) and polyether glycol (Ng210: tetrahydrofuran-oxide propylene copolymer glycol, Mn=1000 g.mol\(^{-1}\), hydroxyl value=110 mg KOH/g) were obtained from Shanghai Chemical Co., China, and were dried for 48 h under a vacuum prior to use. Dehydrated castor oil (DCO) with an OH number of 112 mg KOH/g was prepared in the presence of acid catalysts [11]. Maleic anhydride was obtained from Shanghai Lingfeng Chemical Co., China. Isophorone diisocyanate (IPDI) was obtained from Bayer C.S.: \(\alpha,\alpha\)-Dimethylol propionic acid (DMPA), 1,4-butanediol (BD), N-methyl-2-pyrrolidone (NMP), and triethylamine (TEA) were obtained from Shanghai Aisi Chemical Co., China. Dibutyltin dilaurate (DBTL) and ethylenediamine (EDA) were obtained from Shanghai Chemical Co., China.

Preparation of Maleic Anhydride Modified Castor Oil
Synthesis reaction was conducted in a round bottom, four-necked flask. A weighed amount of castor oil was placed in the reactor and heated to 40ºC with a mild agitation. While keeping the temperature at 40ºC, calculated maleic anhydride which dissolved in butanone was added to the reactor dropwise. Then the reactants were heated to 70ºC for 2 h, after that, the system was heated to 75ºC for 4–5 h. The modified castor oil (MCO) with a hydroxyl value of 112 mgKOH/g and an acid number of 42 mg KOH/g was obtained after evaporating butanone at 85ºC.

Preparation of Aqueous Polyurethane Dispersions
MCO or DCO and Ng210 were charged into the reactor and heated to 120ºC to dehydration under vacuum for 2 h. Then, IPDI and DBTL were added into the reactor dropwise at 60ºC and reacted for about 1 h. After that, BD and DMPA dissolved in NMP were charged into the mixture dropwise and the system was heated to 70ºC for about 2 h to afford NCO-terminated prepolymer. The change of the NCO content during the reaction was determined using a standard dibutylamine back titration method. Upon obtaining the theoretical NCO content, the reaction mixture was cooled to 50ºC and neutralized with TEA for about 30 min. Then the doubly distilled (DDI) water was slowly charged into the PU anionomer under high shear force and the polymer chain was extended by reacting with ethylene diamine. The PU made from MCO and DCO was taken as MCPU and DCPU, respectively. The basic recipes for MCPU and DCPU1.4 are shown in Table 1. The synthesis process of MCPU is presented in Scheme I.

Characterization
The average particle diameters and particle size distributions of MCPU and DCPU1.4 were determined by a BT-9300S particle size analyzer. The viscosity of the dispersions was measured by a Brookfield viscometer at 25ºC.

FTIR Spectra were recorded with Bruker Equinox 55 spectrometer.

The MCPU 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 60ºC for 12 h.

Thermogravimetric experiments were performed on a SDTQ 600 analyzer. Film samples with weighing range between 5 to 7 mg were heated from 30 to 500ºC under N₂ atmosphere at a heating rate of 10ºC/mm.

Differential scanning calorimetric measurements were carried out on a Netzsch DSC 204 thermal ana-
lyzer. The heating rate was 10ºC/min between 100~300ºC under N2 atmosphere.

Wide-angle X-ray diffraction (WAXD) patterns of the MCPU films were recorded on D/max-1200 X-ray diffractometer with CuKα radiation (λ = 1.5405 × 10⁻¹⁰ m), and the samples were examined at 2θ ranging from 5 to 50° at a scanning rate of 5° min.

The mechanical properties of the MCPU films were evaluated by tensile testing. Dumbbell-shaped specimens were prepared by stamping a sheet of the MCPU film with a standard die in accordance with ASTM D638-Type IV. The tensile test was performed at a cross-head speed of 100 mm/min. The tensile strength and elongation-at-break data of each specimen were average of five tests. Hardness of the specimens was measured by Hiroshima Shore A hardness tester.

Each of the MCPU film was cut into 30 mm × 30 mm sample and stored in different solvents. Each sample was removed at a specific interval and weighed until the equilibrium state (no more solvents were absorbed) was reached. The solvent absorptivity (SA%) of the samples was calculated using the following equation:

\[ \text{SA}\% = \left( \frac{W_2 - W_1}{W_1} \right) \times 100 \]

where \( W_1 \) and \( W_2 \) are the initial weight and weight at equilibrium state of the sample, respectively.

### RESULTS AND DISCUSSION

#### Properties of Dispersions

Figure 1 presents the particle size distributions of DCPU1.4 and MCPU1.4 with various NCO/OH molar ratio. Table 2 presents the average particle diameters and viscosities of these dispersions. It shows that the DCPU1.4 dispersion has broader particle size distribution and larger particles than MCPU1.4, which may be probably attributed to the different distributions of ionic groups. In DCPU1.4, the ionic groups are all located in hard segment, while in MCPU1.4, they are located both in soft and hard segments, resulting in

![Figure 1. Particle size distributions for MCPU dispersions and DCPU1.4.](image)
higher compatible between the polymer chains and water.

Figure 1 and Table 2 also show that the particle size distribution broadens and the average particle diameter increases with increasing NCO/OH molar ratio. In PU dispersion, the particle size is mainly governed by the hydrophilicity of PU [12,13]. However, the hydrophilicity decreases with the increase in NCO/OH molar ratio may be related to two parameters. First, as NCO/OH molar ratio increases, the residue of NCO group increases, and therefore, they react with water during dispersion process, resulting in carbamido, and sequentially decrease the flexibility of polymer chain. MCPU with flexible chains are more easily deformed and dispersed into smaller particles in water. Second, the carbamido groups are very polar and they distribute in the surface of the particles and cause the reaction heat to increase, which can heighten the viscosity of the particles and make them easy to stick together and hard to disperse under shear.

Table 2. Average particle diameters and viscosities for MCPUs and DCPU1.4

<table>
<thead>
<tr>
<th>Sample</th>
<th>DCPU1.4</th>
<th>MCPU1.15</th>
<th>MCPU1.4</th>
<th>MCPU1.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersion viscosity (mPa.s)</td>
<td>26.3</td>
<td>54.3</td>
<td>40.2</td>
<td>25.6</td>
</tr>
<tr>
<td>Average particle diameter (nm)</td>
<td>102.4</td>
<td>35.7</td>
<td>79.2</td>
<td>101.6</td>
</tr>
</tbody>
</table>

Figure 2. IR Spectra for MCPU films with various NCO/OH molar ratios.
force, resulting in bigger size particles [14].

In PU dispersion, the ionic groups are located predominantly on the surface of droplets and stabilized by the electrical double layers. With the decrease of the polymer particle size, the relative size of the water layer to total particle size increases. In addition, with the particle size decreasing, there is an increase in the number of particles [15-17]. Hence, the effective hydrodynamic volume of the dispersed phase increases and the force of friction among particles increases, resulting in an increase of viscosity.

IR Spectra

Figure 2 shows IR spectra of MCPU films and the characteristic functional groups for the MCPU films with various NCO/OH molar ratios. The -NH stretching vibration bands are thought to be composed of hydrogen-bonded -NH (3350 cm⁻¹) and free -NH (3500 cm⁻¹), while -C=O bands consist of hydrogen-bonded -C=O (1704 cm⁻¹) and free -C=O(1735 cm⁻¹). In PU, the hydrogen bond is mainly formed by -NH with -C=O in hard segment and the ether-oxygen or the carbonyl of soft segment. In the present case, the free -NH, hydrogen-bonded -NH and -C=O increase with increasing of NCO/OH molar ratio. This is mainly due to the more carbamido groups being formed when NCO/OH molar ratio is higher and the urea groups present two nitrogen atoms suitable to form hydrogen bonds, whereas urethane groups present is only on nitrogen in PU.

DSC

DSC Traces of MCPUs with various NCO/OH molar ratios are shown in Figure 3. Data obtained from the DSC traces of MCPUs and DCPU1.4 are listed in Table 3, where T_g corresponds to soft segment and T_g corresponds to hard segment. It shows that T_g of MCPU1.4 is higher while T_g2 is lower compared to DCPU 1.4, indicating the phase mixing in MCPU1.4 is being increased. This is mainly due to the hydrogen bonding between hard and soft segments which was altered, resulting in harder domains dissolved in soft matrix. It can be observed that T_g1 and T_g2 both increase with increasing of NCO/OH molar ratio. This might be due to more urea groups which were formed at higher NCO/OH molar ratio and they can increase the hydrogen bonding interaction and cohesion both in soft and hard segments. As a result, the mobility of soft segments was limited and the ordering of hard segments increased, as the T_g1 and T_g2 of MCPU1.7 exceeded the T_g1 and T_g2 of MCPU1.15.

From all patterns of Figure 3 we can also see two endotherms at around 75~120°C and 220~230°C that are due to the relaxation processes of long ordered and the melting of microcrystalline of hard segments respectively. It shows that the endotherm shifted to higher temperature and the heat capacity increased increasing NCO/OH molar ratio. This might be due to more and stronger hard-hard segment H-bonding at higher NCO/OH molar ratio acting as physical cross-

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_g1(°C)</th>
<th>T_g2(°C)</th>
<th>T_a1(°C)</th>
<th>∆H_a1</th>
<th>T_a2(°C)</th>
<th>∆H_a2</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCPU1.4</td>
<td>-56.6</td>
<td>63.2</td>
<td>125</td>
<td>5.24</td>
<td>221</td>
<td>6.79</td>
</tr>
<tr>
<td>MCPU1.15</td>
<td>-47.8</td>
<td>58.3</td>
<td>78.2</td>
<td>2.35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MCPU1.4</td>
<td>-45.9</td>
<td>61.0</td>
<td>120</td>
<td>2.114</td>
<td>226.6</td>
<td>5.538</td>
</tr>
<tr>
<td>MCPU1.7</td>
<td>-42.6</td>
<td>72.2</td>
<td>142</td>
<td>3.268</td>
<td>229.8</td>
<td>9.23</td>
</tr>
</tbody>
</table>

a Glass transition temperature; b Temperature of heat absorption peak; c Heat capacity of absorption peak.
links leading to difficult segmental motion of the polymer chain, and resulting in a more significant phase separation [18]. In this case, some more regular hard segments were formed.

**TG/DTG**

TG/DTG Traces of MCPU films with various NCO/OH molar ratios are presented in Figure 4. A three-step degradation was observed in all these PUs. The figures indicate that in the first step a weight loss less than 5% occurs at about 210–240ºC, as a result of releasing trapped solvent and decomposing of some peroxide linkages produced from MCO containing double bond. In the second stage of degradation, a rapid weight loss starts at approximately 250ºC and continues up to 340–360ºC. This decomposition step corresponds to the breaking of urethane and urea bond, and the decomposition temperature shifts to higher temperature as NCO/OH molar ratio increases. It is well established that the isocyanate-based polymers provide their thermostability in the following order [19]: isocyanurate > urea > urethane > biuret > allophanate. In this investigation, the urea content increases when NCO/OH molar ratio increases as more NCO group chains extended with ethylenediamine. The third degradation stage is related to the decomposition of soft segment. It is to be noted from Figure 4 that an increase of NCO/OH molar ratio also can lead to higher thermal stability of this part. This might be due to more hydrogen bonds being formed between the carbonyl in the soft segments and -NH in the hard segments because of the greater polarity of urea groups. The decomposition temperatures at various weight loss percentages and the char residue at 500ºC are summarized in Table 4. This shows that the decomposition temperatures at different percentages of weight loss and char residue are higher at higher

*Figure 4.* TG/DTG Curves for MCPU films with various NCO/OH molar ratios.

**Table 4.** Decomposition temperatures for MCPU films with various NCO/OH molar ratios and charge residues.

<table>
<thead>
<tr>
<th>Degradation (%)</th>
<th>Decomposition temperature (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MCPU1.15</td>
</tr>
<tr>
<td>10</td>
<td>269.8</td>
</tr>
<tr>
<td>25</td>
<td>304.67</td>
</tr>
<tr>
<td>40</td>
<td>322.1</td>
</tr>
<tr>
<td>50</td>
<td>332.4</td>
</tr>
<tr>
<td>60</td>
<td>344.9</td>
</tr>
<tr>
<td>80</td>
<td>375.2</td>
</tr>
<tr>
<td>90</td>
<td>394.67</td>
</tr>
<tr>
<td>Charge residue at 500ºC (%)</td>
<td>1.2</td>
</tr>
</tbody>
</table>
NCO/OH molar ratio. This also implies that the films with higher NCO/OH molar ratio presents higher thermostability and also validates the enhancement of physical cross-linking with the increases of NCO/OH molar ratio.

**WAXD**

Figure 5 shows the X-ray diffraction patterns of MCPU films with various NCO/OH molar ratios. The broad scattering halos between 5° and 40° of 2θ are presented in all samples, which implies that all samples are amorphous at room temperature although there must be some amounts of crystalline phase due to the presence of hard segments. This small amount of crystalline is overshadowed by the presence of long aliphatic hydrocarbon chain of MCO and the hydrogen bonding in PU. As a result, the PUs exhibit overall amorphous character even under higher NCO/OH molar ratio [20].

**Mechanical Properties and Solvent Absorptivity of MCPU Films**

Table 5 shows the mechanical properties and solvent absorptivity of MCPU films with various NCO/OH molar ratios. It can be observed that the increase in NCO/OH molar ratio improved the tensile strength and hardness of the material because there is an increase in the degree of interchain hydrogen bonding, which leads to the formation of more rigid films. However, the higher hydrogen bonding degree restricted the rotation of polymer segments, resulting in decreasing of elongation-at-break. The water and toluene absorptivity decreases with increasing of NCO/OH molar ratio is also mainly attributed to the physical cross-links formed by more hydrogen bonding in higher NCO/OH molar ratio as identified by IR study.

**CONCLUSION**

A series of aqueous anionic PU dispersions with ionic groups in the soft segments were synthesized from a polyether glycol, maleic anhydride modified castor oil, isophorone diisocyanate, and α,α-dimethylol propionic acid according to the prepolymer mixing process. The particle size distribution of aqueous PU dispersion becomes broader and the average particle
size diameter increases as increasing of NCO/OH molar ratio. WAXD of the PU films implies that all the samples are amorphous. The tensile strength and hardness of the PU films increase and solvent absorptivity of films decreases with increase in NCO/OH molar ratio. IR Study shows that the hydrogen bonding increases with the increasing of NCO/OH molar ratio. It is identified that the phase mixing increases when some ionic groups were incorporated in soft segments and phase separation increases with increase in NCO/OH molar ratio, confirmed by DSC. TG/DTG result shows that better thermostability was observed under higher NCO/OH molar ratio. These characteristics can be attributed to formation of thermostable urea groups and more intermolecular hydrogen bonding.

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