



## Aqueous anionic polyurethane dispersions from castor oil

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### ABSTRACT

In this study, dimethylol propionic acid (DMPA) and dimethylol butanoic acid (DMBA) were employed to synthesize the castor oil-based waterborne polyurethane dispersions (PUDs). The effects of these two emulsifier and their contents on the properties of the PUDs as well as their films were investigated systematically. The results show that as the emulsifiers contents increase, the particle size and zeta potential of the PUDs decrease while the tensile strength of the resulting PU films increase but thermal stability, water and chemical resistance decrease. The PUDs from DMBA exhibit smaller particle size than those from DMPA and the films from the former show higher tensile strength, higher elongation at break but lower thermal stability, lower water resistance. This work provides a new way to synthesize environmental friendly bio-based waterborne polyurethanes whose properties can be tuned according to their application, such as coating, ink, leather, styling products and so on.

### 1. Introduction

As a consequence of the increasingly strict environmental legislation and the concern about human health, waterborne polyurethane (WPU) has become one of the most investigated materials in the past decade (Philipp and Eschig, 2012). As an excellent replacement of the solvent based polyurethanes (PUs), WPU exhibits a wide range of advantages. Above all, WPU contains zero or low volatile organic compound (VOC) since water is used as dispersant in these PU products, while solvent PU contains more than 600 g/L of VOC (Burja et al., 2015). Moreover, WPUs avoid combustion or blast in the process of preparation, storage, transportation and painting, meeting the urgent requirement of safety as well as environmental protection. Additionally, several excellent performances are observed for WPU, such as flexibility, good strength, outstanding abrasion resistance etc. (Gurunathan et al., 2013), enabling it widely application in various fields (Kang et al., 2018).

As mentioned above, the environment-friendly characteristics of WPU is usually achieved by introduction of the internal emulsifiers and employing water as dispersant. Internal emulsifiers are diols with ionic groups, including carboxylate, sulfonate, or quaternary ammonium salt, or non-ionic groups like poly (ethylene oxide) (Honarkar et al., 2015). The ionic groups in the emulsifier are hydrophilic in nature, providing surface charge to disperse hydrophobic PU segments in water. Consequently, the emulsifiers play an important role in influencing the properties of both the polyurethane dispersions (PUDs) and the

resulting films.

Dimethylol propionic acid (DMPA), and dimethylol butanoic acid (DMBA) are typical commercial available emulsifiers used in anionic PUDs. Their OH groups are more reactive than the COOH group due to the steric effect, resulting in the preferential reactivity between OH groups and isocyanates to form long PU chains while the COOH groups provide surface charge after neutralization and stabilize PUDs in the water phase (Chen et al., 2014). Many research groups have used DMPA or DMBA as emulsifiers for WPUs due to the outstanding mechanical properties of the resulting films. Philipp et al. prepared a series of WPUs derived from rapeseed fatty acid methyl esters with 1.3–5.0 wt% DMPA. Their results demonstrated that increasing DMPA content decreases the particle size of the PUDs but also reduces the hydrophobicity of the films (Philipp and Eschig, 2012). Lee et al. synthesized WPUs from polytetramethylene ether glycols with 2 ~ 3 wt% DMBA, which exhibit tensile strength from 6.5 to 10.5 MPa (Lee and Kim, 2009). Lee and his co-workers compared the properties of the WPUs from three kinds of polycarbonatediols with various carboxylic diols, including DMPA, DMBA and carboxylic polycaprolactonediol (L4672, L6002, and L5652). They found that the similar particle sizes were observed for both the PUDs from DMBA and DMPA, but the former films exhibit a higher tensile strength and a lower elongation at break (Lee et al., 2009).

Recently, the utilization of bio-based polyols as a replacement of petroleum based counterparts for WPU has attracted much attention

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due to their ecofriendly nature and versatile properties. As an abundantly available, low-cost and renewable raw material, castor oil is widely used in coatings, sealants, adhesives and paints etc. (Kong et al., 2013). In addition, castor oil contains active hydroxyl groups, which can react with isocyanates directly without further modification (Nguyen Dang et al., 2016). The specific hydrophobic triglyceride structure of castor oil can also improve the mechanical properties, water and chemical resistance of the resulting WPU films (Bullermann et al., 2013). Luong et al. demonstrated that the incorporation of castor oil as soft segment in polymer chain significantly altered the mechanical properties and flexibility of the films, which exhibit a maximal elongation at break of about 1200%. Furthermore, the thermal and mechanical properties of the PU films can be tailored by controlling the ratios between castor oil, poly(dimethylsiloxane) and poly(tetrahydrofuran), which were both used as soft segments in the polymer preparation (Nguyen Dang et al., 2016). The castor oil based anionic WPU prepared by Xia et al. exhibits a relatively high tensile strength of 13 MPa and elongation at break of 336% (Xia and Larock, 2011). Gurunathan and Chung successfully synthesized a series of WPU nanocomposites from castor oil with 0 ~ 5 wt% silicon. The results show that the film without silicon also has a considerably low water absorption of 7.2 wt% (Gurunathan and Chung, 2016).

Although DMPA and DMBA were employed in many studies as the emulsifier to prepare PUDs (Wang et al., 2015), there is considerable ambiguity about the properties difference between the castor oil based WPUs from these two kinds emulsifiers, and the emulsifier contents' impact on the thermal and mechanical properties of the resulting PU films. In this study, castor oil-based WPUs were synthesized with two emulsifiers (DMPA and DMBA) and a variable ratio between the OH groups in CO, the NCO groups in IPDI, and the OH groups in the emulsifier (1:1.7:0.69; 1:1.85:0.84; 1:2:0.99; 1:2.2:1.19). Centrifuge and zeta-sizer were used to characterize the stability of the PUDs, while tensile electronic universal testing machine, dynamic mechanical analyzer, thermal analyzer were used to investigate the thermo-mechanical properties of the films.

## 2. Material and methods

### 2.1. Materials

Castor oil (OH number: 164 mg KOH/g) was purchased from Fuyu Chemical Co. Ltd. Isophorone diisocyanate (IPDI) was purchased from Wengjiang Chemical Reagent Co. Ltd. Dimethylol propionic acid (DMPA) and dimethylol butanoic acid (DMBA) were provided by Beijing Bailingwei Technology Co. Ltd. Dibutyltin dilaurate (DBTDL) was purchased from Fuchen Chemical Reagent Factory. Triethylamine (TEA) was purchased from Aladdin reagent. Methyl ethyl ketone (MEK) was provided by Tianjin Hongda Chemical reagent. All materials were used as received without further purification.

### 2.2. Preparation of castor oil-based anionic waterborne PUDs

Figure 1 shows the preparation of anionic WPU dispersion from castor oil. Castor oil (6 g), IPDI and DMPA (or DMBA) were introduced into a dried double neck flask and stirred (130–170 r/min) at 78 °C for 10 min to obtain a homogenized mixture. Then two drops of DBTDL were added as catalyst. When the mixture almost can't flow, MEK (30 ml) was added to reduce the viscosity of the pre-polymer. After reaction for another 2 h, the mixture was cooled to room temperature. Then TEA was added to neutralize free COOH in the polymer chain under stirring for 30 min. Finally, the stirring rate was elevated to 300 r/min and the polymer was dispersed in 90 ml water for 2 h. The PUDs with solid content ranging from 10.6 to 12.5 wt% were obtained after removal of the MEK by rotary evaporation (Table 1).

### 2.3. Characterization

All the samples were centrifuged at 3000 r/min for 30 min on a Tomos 3–18 Centrifuge to evaluate their stability. The zeta potential, average particle size and particle size distributions of the samples were obtained on a Zeta-sizer Nano ZSE (Malvern Instruments) at 25 °C. The samples were diluted with DI water to about 0.01 wt% before test.

The PU films used in further analysis were obtained by casting the PUDs in glass molds and dried at room temperature for 4 days. All the films were further dried at 60 °C in oven for 24 h to remove the residual water before test.

The tensile properties of the PU films were measured on an electronic universal testing machine (Shimadzu AGS-X) with an extension rate of 100 mm/min. Rectangular specimens of 40 mm × 10 mm (length × width) were used. More than three replicates of all the samples were taken in the test and the data were recorded as mean ± standard deviation.

The dynamic mechanical behavior of the castor oil based PU films was measured by a dynamic mechanical analyzer (Netzsch DMA 242C) with a temperature range from –60 to 120 °C and heating rate of 5 °C/min in tensile mode at 1 Hz. Rectangular specimens with a width of 6 mm and a length of 25 mm were used.

The thermo-gravimetric analysis of the PU samples was carried out by a Netzsch- STA 449C thermal analyzer. All the samples (8–14 mg) were heated under nitrogen from 30 to 700 °C with a heating rate of 20 °C/min.

The hydrophobicity of the films was assessed by measuring the surface wettability of the films using a contact angle goniometer (Powereach JC2000C1). Water and ethanol contact angle of the samples were both measured at room temperature by the sessile-drop method.

The water resistance properties of the resulting films were characterized to further evaluate the hydrophobicity of the samples. The dried films of 10 mm × 10 mm (length × width) were immersed in deionized water for 56 h. The weights of the samples before and after immersion were measured. The water absorption ratios of the samples were calculated by following equation: Where  $m_0$ ,  $m_1$  represent the weights of the films before and after immersing in the water. Average values of at least four replicates of each sample were taken.

## 3. Results and discussion

### 3.1. Difference in reactivity of the emulsifiers

The reaction between NCO group and DMBA exhibits a higher rate than that between NCO group and DMPA. It takes about 15 min for the prepolymerization with DMBA to reach the gel point before the addition of the MEK, while it takes about 1 h for the systems with DMPA. Two main factors are associated with the difference in reaction rate. On one hand, the higher melting point and lower solubility (MEK) of DMPA ( $T_m = 185\text{--}190\text{ }^\circ\text{C}$ ; 20 °C,  $S(\text{DMPA}) = 0.4\text{ g}/100\text{ g MEK}$ ) than DMBA ( $T_m = 108\text{--}113\text{ }^\circ\text{C}$ ; 20 °C,  $S(\text{DMBA}) = 7\text{ g}/100\text{ g MEK}$ ) leads to a lower collision rate between DMPA and isocyanate (Fernandes et al., 2015; KosheelaDevi et al., 2016). On the other hand, the extra methylene ( $-\text{CH}_2-$ ) in the side chain of DMBA decreases the steric hindrance for the reactions between its OH groups and NCO groups in IPDI (the structural formula of DMPA and DMBA are shown in Fig. 1).

### 3.2. Properties of the PUDs from different emulsifiers

The appearances and particle size distribution of the PUDs from different emulsifiers are presented in Figs. 2 and 3, respectively. The average particle sizes and zeta potentials data are summarized in Table 2. It can be found that the PUDs from DMPA exhibit relatively larger particle sizes and deeper color appearance (opalescent) as well as lower transparency than those from DMBA when the same molar ratios

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