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Castor oil-based cationic waterborne polyurethane dispersions: Storage stability, thermo-physical properties and antibacterial properties

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ABSTRACT

In this study, castor oil and its derivative were used to prepare cationic waterborne polyurethane dispersion using N-methyl diethanolamine (MDEA) as ion center. The effect of polyol functionalities and the ionic chain extender contents on the particle size and antibacterial properties of the polyurethane dispersions, and thermo-mechanical, thermal stability, mechanical properties, water/solvent uptakes of the resulting polyurethane films were thoroughly investigated. Moreover, all the polyurethane dispersions exhibit enhanced antibacterial activity against *Vibrio parahaemolyticus* with the rise of MDEA content and the reduction of polyol functionalities, but rarely antibacterial activity to *Listeria monocytogenes*. To the best of my knowledge, this work for the first time extensively investigate the structure-property relationships of castor oil based cationic waterborne polyurethane dispersions and their polyurethane films.

1. Introduction

Polyurethanes (PUs) are one of the most versatile polymers and have been widely used in various fields such as coatings, adhesives, clothing, paints and foams because of their excellent chemical resistance, tunable thermo-mechanical properties and good process ability. (Gurunathan et al., 2013; Schmidt et al., 2017) However, traditional polyurethane products usually contain large amount of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs), which are mostly released into the air during practical application, leading to a big health threat for producers and users. With the introduction of increasingly strict legislation and consumer demands towards reducing the VOC and HAPs, a current renaissance of environmentally friendly waterborne polyurethanes has occurred in a global scale, aiming to partially or completely replace solvent-based polyurethanes for application in ink, adhesives and coatings. (Gogoi and Karak, 2014)

In order to disperse polyurethanes in aqueous as a stable phase, hydrophilic groups (carboxylic and sulfonic acid, amine) are usually incorporated into the side chain or backbone of the polymers, which leads to the formation of waterborne polyurethanes. Much progress have been made recently to formulate waterborne polyurethanes with high solid content and high performance. (Burja et al., 2015; Peng et al., 2015; Peng et al., 2014; Zhang et al., 2015) For example, Li and his co-workers synthesized a cationic waterborne polyurethane with a high solid content (42.06–52.18%) via the combination of cationic ionic (N-methyl diethanolamine) and nonionic segments (Poly(oxyethylene alkyl amine)). (Li et al., 2017) Yong et al. have synthesized a solvent-free and chemical matt waterborne polyurethanes, simultaneously using sulfonic (sodium 2-[(2-amino ethyl) amino] ethane sulfonate) and carboxylic acid (2,2-Bis(hydroxymethyl) pro-pionic acid) as hydrophilic chain extender (Yong et al., 2015). And Yu et al. successfully prepared a series of high waterproof carboxylic acid type waterborne polyurethane films with introduction of fluorine and siloxane to increase the cross-linking density of the materials. (Yu et al., 2016)

Up to date, most of the raw materials (Polyols, isocyanates, chain extenders) used for polyurethane dispersions (PUDs) are derived from petrochemical feedstock, which are widely regarded as nonrenewable and major source of criteria air pollutants. (Alam et al., 2014; Zhu et al., 2016) With the depletion of the world crude oil stock and increasing environmental concerns, efforts on a global scale are dedicated to find a renewable resource (such as cellulose, natural oils, lignin, and so on) for bio-based polyurethanes to replace petroleum based counterparts. (Gaikwad et al., 2015; Zhang et al., 2014) Vegetable oils as a kind of typical renewable biomass resources are among the most promising for polyol synthesis due to its low cost, and readily available. (Pawar et al., 2015) Vegetable oils are triglyceride of fatty acid that usually bears 12–22 carbon atoms and 0–3 carbon–carbon double bonds. Except for castor oil, most vegetable oils do not contain hydroxyl groups.

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(Gurunathan et al., 2015) The reactive ester and carbon–carbon double bonds in triglyceride oils offer several routes to introduce hydroxyl groups necessary in polyols for PU synthesis, including epoxidation/ring opening, ozonolysis/reduction, hydroformylation/reduction, transesterification, thiol-ene click reactions. (Bullermann et al., 2013; Feng et al., 2017; Zhang et al., 2013)

Anionic and cationic PU dispersions have been synthesized from different vegetable oil based polyols. It is found that the hydrophobic nature of triglycerides and long fatty acid chains endow the resulting PU films excellent chemical and physical properties, including enhanced hydrolytic, flexibility and toughness. (Zhang et al., 2017) Lu et al. successfully prepared soybean oil-based cationic waterborne PU films with tensile strengths from 5.7 to 23.2 MPa and elongation at break from 235 to 291%. Moreover, the effect of polyols functionalities on the size of the polyurethane particle and the thermo-mechanical properties of the PU films were studied and discussed. (Lu and Larock, 2010) Fu and his co-worker synthesized a castor oil-based anionic waterborne PU film with a high flexibility (1 mm) and excellent chemical resistance (1.75% water absorption and 90% toluene absorption for 168 h). (Fu et al., 2014) Saalah et al. investigated the effect of the OH number, DMPA content and hard segment content on the stability of the anionic waterborne PU dispersions from jatropha oil, as well as the physical, mechanical and thermal properties of the resulting films. The resulting PU film exhibited excellent hydrophobicity, with a contact angle of 90° or more, indicating a nonwetting surface. (Saalah et al., 2015) To the best of my knowledge, the effect of polyols functionalities and chain extender content on the size of the anionic polyurethane particle and the thermo-mechanical properties of the resulting films have been widely investigated. But their effects on the performance of castor oil-based cationic polyurethane have not been reported previously.

In this study, cationic waterborne PUDs were successfully prepared from castor oil and its derivative using N-methyl diethanolamine (MDEA) as ion center. The effect of polyol functionalities and MDEA contents on the physical properties and antibacterial properties of the PUDs and the thermo-mechanical properties of the resulting films were investigated. The particle size and zeta potential of the PUDs were characterized by zeta-sizer while the thermo-mechanical properties of the resulting PU films were characterized by DMA, TGA, tensile testing. In addition, the antibacterial properties of the resulting PUDs were tested against *Vibrio parahaemolyticus* and *Listeria monocytogenes*. The work extensively investigated the structure-property relationships of castor oil based cationic waterborne polyurethane dispersions and their films.

2. Experimental

2.1. Materials

Castor oil (OH number: 164 mg KOH/g) and its derivative (OH number: 208 mg KOH/g) were provided by Fuyu Chemical Company, and Guangzhou Xinye Trading Company, respectively. In this study, they are coded as castor oil-164, and castor oil-208. Isophorone diisocyanate (IPDI) and N-methyl diethanolamine (MDEA) were purchased from Wengjiang Chemical Reagent Company. Dibutyltin dilaurate (DBTDL) was purchased from Fuchen Chemical Reagent Factory. Acetic acid, and methyl ethyl ketone (MEK) were purchased from Aladdin reagent and Tianjin Hongda Chemical reagent, respectively. All materials were used as received without further purification.

2.2. Preparation of castor oil-based waterborne PUDs

Firstly, castor oil (6 g) and IPDI were mixed in a double neck round bottom flask equipped with mechanical stirrer for 10 min at 78 °C. One drop of DBTDL was added in the mixture to allow the reaction to proceed for 10 min. Then, MDEA was added under high-speed stirring.

Table 1
Compositions of the waterborne PUs.

Samples	OH number of castor oil (mg KOH per g)	Molar ratio		
		NCO	OH[a]	OH[b]
PU164-0.69	164	1.7	1	0.69
PU164-0.84	164	1.85	1	0.84
PU164-0.99	164	2.0	1	0.99
PU164-1.19	164	2.2	1	1.19
PU208-0.69	208	1.7	1	0.69
PU208-0.84	208	1.85	1	0.84
PU208-0.99	208	2.0	1	0.99
PU208-1.19	208	2.2	1	1.19

[a] Hydroxyl molar ratio of castor oil.
[b] Hydroxyl molar ratio of the MDEA.

The molar ratio of the raw materials is summarized in Table 1. After the reaction continued for 30 min, 30 ml MEK was added to reduce the viscosity. The mixture continued to react under stirring for 2 h at 78 °C. After the reactants were cooled down to room temperature, acetic acid was added as neutralizer under stirring for 30 min. Finally, 90 ml distilled water was added for emulsification for 2 h. The waterborne PUDs with a solid content of 10–12 wt% was obtained after MEK was removed by rotary evaporator. The PU films were obtained after their corresponding waterborne PUDs were casted and dried in a silicon mold at room temperature for at least 48 h (See Scheme 1).

2.3. Characterization

The stability of waterborne PU dispersion was evaluated by centrifuging the emulsion at 3000 r/min for 30 min on Tomos 3–18. A Zeta-sizer Nano ZSE (Malvern Instruments) was used to measure the size distribution and zeta potential of the PU dispersions which was diluted with distilled water to about 0.01 wt% before test.

The mechanical properties of the WPU films were determined using an electronic universal testing machine (UTM-4204) with a crosshead speed of 100 mm/min. The waterborne polyurethane dispersions were casted into a silicon mold and allowed them dry in room temperature for PU films. All the samples with a length of 30 mm and a width of 10 mm were dried at 60 °C for 12 h before test. An average value of at least three replicates of each PU sample was taken.

The dynamic mechanical behavior of the resulting films was determined using a Netzsch DMA 242C dynamic mechanical analyzer in tensile mode at 1 Hz. The samples with a length of 8 mm and a width of 6 mm were heated from −60 to 120 °C at a rate of 5 °C min^{-1}. For this study, the glass transition temperatures (T_g) of the PU films were obtained from the peaks of the loss factor curves.

Thermo-gravimetric analysis (TGA) of the PU films was carried out on a Netzsch- STA 449C thermal analyzer. The samples were heated from 30 to 700 °C at a heating rate of 20 °C min^{-1} in a nitrogen atmosphere. Generally, 8–14 mg samples were used for the test.

The chemical resistance of the PU films against distilled water and ethanol was conducted according to the methods previous reported (Wang et al., 2015a; Xia and Larock, 2011). All the square films with a length of 10 mm were dried at 60 °C for 12 h before test. An average value of more than four replicates of each sample was taken. The PU films with known weight (m_0) were immersed in a distilled water bath at room temperature for 20 days for water absorption. It was also immersed in absolute ethanol for 96 h for ethanol uptake. Then the films were weighed (m_1) and dried at 60 °C for at least 48 h. The dried films were then weighed (m_2) and the percentage of water absorption (W_A), ethanol absorption (W_E), and weight losses (W_x, W_y) of the resulting films in water and ethanol were calculated as follows:

$$W_A(\%) = \frac{(m_1 - m_0)}{m_0} \times 100\%$$