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Synthesis and properties of high-functionality hydroxyl-terminated polyurethane dispersions

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ABSTRACT

High-functionality hydroxyl-terminated polyurethane aqueous dispersions (OH-PUDs) were synthesized with sulfonic polyester diol as hydrophilic chain extender, and alcohol-amine compounds as end-cappers. Two-component waterborne polyurethane (2K-WPU) films based on OH-PUDs were prepared and characterized by ultraviolet-visible spectrophotometer and surface contact angle measurement. The effects of synthesis process, molar ratio of NCO/OH, type and molecular weight of macro-diol, and the category of alcohol-amine capping agents on the properties of OH-PUDs and 2K-WPU films were investigated. OH-PUD obtained from "first dispersing then blocking PU prepolymer" preparation process displayed the best storage stability. The water-resistance of 2K-WPU film was greatly improved with increasing the average functionality of OH-PUDs, and then OH-PUDs displayed good comprehensive properties with PCL220 as the soft segment, trometamol (Tris) as the end-capper and with 1.5 of NCO/OH molar ratio. The 2K-WPU film prepared from OH-PUD-3 exhibited good water-resistance, good transparency and high hardness.

1. Introduction

Two-component waterborne polyurethane (2K-WPU) has attracted increasing interesting due to their high performance and very low volatile organic compounds (VOC) contents [1–4]. In general, 2K-WPU consists of aqueous hydroxyl resins (emulsion or dispersion) and water-dispersible polyisocyanates (WDPs) [5]. On the aspect of aqueous hydroxyl resins, hydroxyl resin aqueous dispersion, including polyacrylate polyol dispersion (PAD), polyester polyol dispersion (PED) and hydroxyl-terminated polyurethane dispersion (OH-PUD) has received great attention due to possesses good dispersion stability and good film appearance [6,7]. However, PAD usually exhibits some disadvantages including low solid content, high viscosity, and then its 2K-WPU film always possesses slow drying speed and poor water-resistance. PED carrying ester groups is easily to hydrolyze during the storage and service, and its 2K-WPU film usually exhibit poor water-resistance. Compared with PAD and PED, OH-PUD possesses some advantages including easy designing of the molecule structures and adjustable content of soft segments, and the 2K-WPU films display good wettability, excellent appearance and good physic-chemical properties [7,8]. As a consequence, OH-PUD is the most promising hydroxyl resin dispersions for 2K-WPU.

In the first few years, OH-PUDs were synthesized by so called "pseudo one-step" methods [5,9], namely, using excess diol to block NCO groups of PU prepolymer followed by neutralization and dispersion. These OH-PUD always possess big particle sizes and poor storage stability owing to the high viscosity of the prepolymer [11,12], and low average hydroxyl functionality made their 2K-WPU films exhibiting poor water- and solvent-resistance as well as other film properties [7,8,10]. To solve these problems, the "post-capping method" was introduced. Zhang et al. [13] prepared OH-PUD through diethanolamine (DEA) or ethylenediamine (EDA) reacting with the isocyanate-terminated prepolymer to introduce −OH groups into PUD chains. However, these OH-PUD still got low hydroxyl functionality and contents as the isocyanate-terminated prepolymer tended to priority react with EDA, lead to the DEA or DEA contents was not enough in the PU chains. Very recently, Liu et al. [14] provided a new method. Generally, isocyanate-terminated prepolymer were prepared, neutralized and EDA chain extended, then it was added to trometamol aqueous solution with vigorous stirring to prepare OH-PUD. The water-resistance of 2K-WPU film was indeed improved. However, the viscosity of prepolymer would sharply increase after neutralization and EDA chain extension, so that the prepolymer was difficult to be dispersed stably. In order to receive stable dispersions, a large amount of water should be added to the system, which would dramatically decrease the solid contents of OH-PUD. Meanwhile, the hydrophilic chain extender dimethylol propionic acid (DMPA) was generally dissolved in N-methylpyrrolidone (NMP), which introduced toxic organic solvent to increase the VOC contents. As

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Nomenclature

2K WPU	Two-component waterborne polyurethane
DEA	Diethanolamine
DGA	Diglycolamine
DMPA	Dimethylol propionic acid
EDA	Ethylenediamine
EGA	N-ethyl glucamine
GA	Glucosamine
IPDI	Isophorone diisocyanate
NMP	N-methylpyrrolidone
n(NCO)/n(OH)	Molar ratio of −NCO and −OH
OH-PUD	High-functionality hydroxyl-terminated polyurethane aqueous dispersions
PAD	Polyacrylate polyol dispersion
PED	Polyester polyol dispersion
S-N1	OH-PUD prepared with N210
S-N2	OH-PUD prepared with N220
S-PBA2	OH-PUD prepared with PBA220
S-PCL2	OH-PUD prepared with PCL220
S-PCDL2	OH-PUD prepared with PCDL220
SPED	Sulfonic polyester diol
S-PTMEG2	OH-PUD prepared with PTMEG220
Tris	Trometamol
WDP	Water-dispersible polyisocyanate
ω(TMP)	Mass percentage of TMP
ω(SPED)	Mass percentage of SPED
ω(soft)	Mass percentage of soft segments

a result, the strategy to increase the hydroxyl functionality and solid contents of OH-PUDs is currently key issue for 2K-PUDs [15–17].

Toward this end, in this work, we synthesized several hydroxyl-terminated polyurethane dispersions through a series of alcohol-amine compounds with different hydroxyl functionality as end-cappers. We investigated the effects of synthesis process, molar ratio of NCO/OH, type and molecular weight of macro-diol, and the categories of end-cappers on the properties of OH-PUDs and 2K-WPU films. The high-performance 2K-WPUs with high solid content, hardness, good transparency and resistance were also prepared.

2. Experimental

2.1. Materials

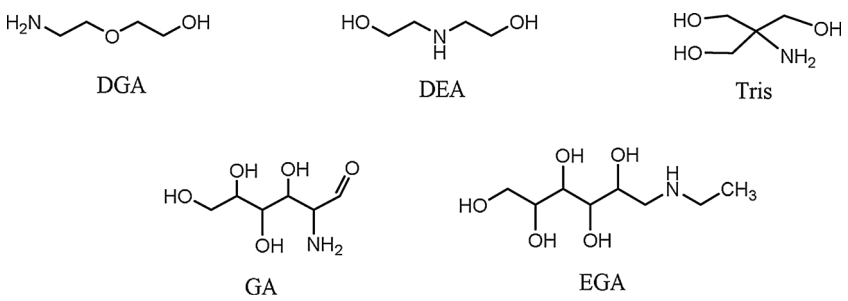
Isophorone diisocyanate (IPDI) was offered by Degussa-Hess (Germany). Polyether diol (N220, M_n = 2000 g/mol, N210, M_n = 1000 g/mol), polycaprolactone diol (PCL220, M_n = 2000 g/mol, PCL210, M_n = 1000 g/mol), polytetramethylene-ether glycol (PTMG220, M_n = 2000 g/mol, PTMEG210, M_n = 1000 g/mol) and 1,4-butanediol (BDO) were obtained from Perstorp Group (Sweden). Polybutylene adipate diol (PBA220, M_n = 2000 g/mol, PBA210, M_n = 1000 g/mol) and polycarbonate diol (PCDL220, M_n = 2000 g/mol, PCDL210, M_n = 1000 g/mol) were purchased from Asahi Kasei Corporation (Japan). Sulfonic polyester diol (SPED, M_n = 550 g/mol) was supplied by Beijing Baiyuan Chemical Co., Ltd. (Beijing, China). Ethylenediamine (EDA), diethanolamine (DEA) and acetone were purchased from Guangzhou Petrochemical Company (Guangzhou, China). Water-dispersible polyisocyanate (Bayhydur XP2487, 100% solid content, NCO% = 20.6%) was obtained from Bayer (Germany). Diglycolamine (DGA), trimethylol propane (TMP), trometamol (Tris), glucosamine (GA) and N-ethyl glucamine (EGA) were supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). The catalyst consisted of 50% silver catalyst and 50% organic bismuth catalyst, which was provided by Seho Tech Inc. (Korea). All the materials above were used without further purification. Scheme 1 describes the structures of alcohol-amine compounds.

2.2. Synthesis of OH-PUD

Macro-diol (120 g, 0.06 mol), IPDI, SPED (21 g, 0.038 mol), acetone (18 g, 0.31 mol) and catalyzer (0.09 g) were charged into a four-necked flask equipped with mechanical stirrer, nitrogen inlet, thermometer, and condenser. The flask was transferred into a thermostat oil bath and stirred at 70 °C. The −NCO group content of the reaction system was detected according to ASTM D1638. Until reaching to the theoretical value of NCO%, the calculated amount BDO and TMP (12 g, 0.089 mol) solution in acetone (27 g, 0.46 mol) was added within 40 min. Upon reaching the theoretical value of NCO%, the prepolymer was diluted with acetone (45 g, 0.77 mol) and transferred into the scattered machine followed by dispersion in water and chain extension using EDA (the mole ratio of EDA to the theoretically residual NCO was 1:5) as the reported process [18,19]. After removing acetone, the OH-PUDs with about 46 wt% solid contents were obtained. OH-PUDs were prepared with alcohol-amine compounds added in the synthesis progress of prepolymer, before the dispersion step, in the dispersion progress, after the dispersion step and after chain-extension by EDA, respectively. OH-PUD samples were labeled as OH-PUD-0, OH-PUD-1, OH-PUD-2, OH-PUD-3, OH-PUD-4 correspondingly. It should be noted that the alcohol-amine compounds were dissolved in water (54 g, 3 mol) and then added under 25 °C within 10 min in OH-PUD-1, OH-PUD-2, OH-PUD-3, OH-PUD-4. Taking OH-PUD-3 for example, the synthesis routes of OH-PUD with Tris as end-capper is described in Scheme 2. The final molar ratio of −NCO and −OH was defined as n(NCO)/n(OH), and the mass percentage of the soft segments, TMP and SPED were recorded as (soft), (TMP) and (SPED), respectively.

2.3. Preparations of 2K-WPU films

OH-PUDs was mixed with commercially water-dispersible polyisocyanate Bayhydur XP2487 according to 1.3 of the molar ratio of NCO/OH. The mixture was stirred and homogenized by hand for 5 min



Scheme 1. Structures of alcohol-amine compounds (end-cappers).