



Synthesis and characterization of waterborne polyurethane dispersions with different chain extenders for potential application in waterborne ink



Liang Lei, Li Zhong*, Xiaoqiong Lin, Yuanyuan Li, Zhengbin Xia

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

HIGHLIGHTS

- Actual maximum chain extension degree is approximately 60%.
- Diethylene triamine (DETA) is an effective chain extender and crosslinker.
- Chain extenders of ethylene diamine and DETA with a mole ratio of 2:3 are optimal.
- Stable waterborne polyurethane is obtained without removing the organic solvent.
- Synthesized waterborne polyurethane can be directly used as an aqueous ink binder.

ARTICLE INFO

Article history:

Received 3 January 2014
Received in revised form 1 May 2014
Accepted 12 May 2014
Available online 17 May 2014

Keywords:

Waterborne polyurethane
Chain extension
Diethylene triamine
Binder
Waterborne ink

ABSTRACT

Waterborne polyurethane (WPU) dispersions with different amine chain extenders, including ethylene diamine (EDA), diethylene triamine (DETA), and triethylene tetramine (TETA), were synthesized, and the effects of these chain extenders and the NCO/OH molar ratio on the properties of WPU dispersions were investigated. The results revealed that the chain extension mainly occurred on the particle surface and the actual maximum chain extension degree was approximately 60%. All the synthesized WPUs had a lower degree of crystallinity, and the post-chain extension promoted phase separation between soft and hard segments in polyurethane. The trifunctional DETA chain-extended WPU had better thermal stability and adhesion strength, which indicates that DETA is an effective chain extender that can be used for the performance improvement of WPU. Moreover, the chain-extended WPU by EDA and DETA with a mole ratio of 2:3 showed excellent properties. It was also revealed that the NCO/OH molar ratio of 1.6 was appropriate for the preparation of stable WPU dispersion with solid content of about 40 wt% and organic solvent content of 5 wt%. The obtained WPU dispersion could be directly used as a waterborne ink binder without removing the organic solvent, which is conducive to the industrialized production of WPU dispersion and avoids the cost of organic solvent recovery.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

As the versatile environmentally friendly materials, waterborne polyurethanes (WPUs) have gained increasing interest in a broad range of applications owing to their excellent elasticity, abrasion resistance, flexibility, and broad substrate suitability [1–4]. For instance, WPUs have been widely used in adhesives for numerous flexible substrates, such as plastic film, leather, textile, paper, and rubber [5,6]. In the field of flexible packaging printing ink, WPU offers an efficient alternative to the solvent-based polyurethane binder, which is still widely used in the market.

However, most WPUs are linear thermoplastic polymers and have a relatively low average molecular weight. Therefore, some properties of WPUs, such as water resistance, solvent resistance and mechanical property, are inferior to that of solvent-based polyurethanes [7,8]. Crosslinking modification is one of the most important methods used in improving these properties of WPUs. Crosslinking modification involves one-component and two-component crosslinking. For the two-component crosslinking system, a crosslinker as the second component is added to WPUs just before the application to react with the active groups in WPU molecular chains at room temperature. The common crosslinkers for WPUs mainly include carbodiimide [9,10], polyaziridine [8,11], and isocyanate [12–14]. Two-component crosslinking can greatly improve the properties of WPUs. However, the package,

* Corresponding author. Tel.: +86 20 87113773; fax: +86 20 87112093.
E-mail address: celzhong@scut.edu.cn (L. Zhong).

transportation, and construction of the two-component crosslinking system are not convenient and its pot-life is limited [15]. By comparison, the one-component crosslinking system is highly advantageous during the production and application of WPU. So, it is extensively studied and applied in practical products.

One of the most important and pragmatic one-component crosslinking modifications for WPU is the internal crosslinking. The commonly used inner crosslinking agents are those with functionalities greater than two, mainly including hexamethylene 1,6-diisocyanate trimer (HDI trimer), trimethylolpropane (TMP), and diethylene triamine (DETA). HDI trimer and TMP with polyfunctional —N=C=O (NCO) groups and —OH groups, respectively, are added into the reaction mixtures during the synthesis of polyurethane prepolymer to form a cross-linked network or branched-chain structure. In those cases, the obtained prepolymer often has a high viscosity and is difficult to be dispersed in water. To reduce the viscosity of the prepolymer, more organic solvents should be added into the reaction mixtures during the synthesis process, which increases the cost of solvent recovery. In order to resolve this problem, the WPU with low solvent content or solvent-free WPU has gained increasing attention [16,17].

Compared with the internal crosslinking during the synthesis of polyurethane prepolymer, the post-chain extension and crosslinking with the multifunctional amine chain extenders after the emulsification of prepolymer in water can decrease the consumption of organic solvents because of the relatively low viscosity of the prepolymer. Some studies have been conducted on the effects of post-chain extension on the properties of aqueous polyurethane [18–26]. Jhon et al. [18] demonstrated that the amount of residual NCO groups on the particle surface and the required amount of chain extender for optimum chain extension decreased as the total surface area of aqueous polyurethane particle decreased. Moreover, the adhesive strength increased to the point of maximum value of chain extension and then decreased after that point, which indicated that excessive amounts of chain extenders had an unfavorable influence on the adhesive strength. Kwak et al. [23] studied the effect of the chain extender hydrazine monohydrate (HD), ethylene diamine (EDA), and 1,4-butane diamine (BDA) on the properties of waterborne polyurethane-urea anionomers. The results showed that particle sizes, storage modulus, thermal degradation onset temperatures, and tensile strength of samples increased in the order of $\text{BDA} > \text{EDA} > \text{HD}$. The mechanical strength, water resistance, and acetone resistance of the waterborne polyurethane film prepared with trifunctional DETA were higher than that prepared with EDA [26].

However, most studies were mainly related to diamine chain extenders, and little effort was directed toward the effects of post-chain extenders with functionalities greater than two on the properties of WPU. In this study, the WPU with different types and amounts of multifunctional post-chain extenders, including EDA, DETA and triethylene tetramine (TETA), were synthesized (Scheme 1). The properties of WPU, such as particle size and distribution, molecular weight, crystallinity, thermal and mechanical property, steaming and boiling resistance, and adhesion were studied. The WPU dispersion with organic solvent content of 5 wt% was also studied.

2. Experimental

2.1. Materials

Polycaprolactone diol (PCL, $M_w = 2000$) (supplied by YIP'S CHEMICAL, HK) was used as macroglycol, and it was dried at 120 °C under vacuum for 2 h to remove residual water. Isophorone diisocyanate (IPDI) and 2,2-dimethylolpropionic acid (DMPA) were

used without further purification and also provided by YIP'S CHEMICAL. 1-methyl-2-pyrrolidinone (NMP, Fuchen, China), triethylamine (TEA, Lingfeng, China), 1,4-butanediol (BDO, Kermel, China), ethylene diamine (EDA, Lingfeng, China), diethylene triamine (DETA, Fuchen, China), and triethylene tetramine (TETA, Fuchen, China) were all purchased in AR grade. Deionized water was used as the dispersing phase.

2.2. Synthesis of the waterborne polyurethane dispersions

Waterborne polyurethane dispersions were prepared by the prepolymer mixing process as shown in Scheme 1. Firstly, PCL and DMPA dissolved in NMP were added into a four-neck flask equipped with a mechanical stirrer, thermometer, condenser and nitrogen gas inlet, and heated at 70 °C with stirring for 30 min to obtain a homogeneous mixture. IPDI was then added into the homogenized mixture and stirred under nitrogen atmosphere until the amount of residual NCO groups reached the desired value (determined by dibutylamine back titration). Then, BDO dissolved in acetone was dropwise added into the reactor for 30 min and the reaction proceeded at the constant temperature until the theoretical NCO groups content was reached. Afterwards, the obtained NCO-terminated prepolymer was cooled down to 60 °C and neutralized by TEA (DMPA equiv). Subsequently, the prepolymer solution was emulsified with a certain amount of deionized water to obtain a waterborne polyurethane dispersion. The post-chain extension was carried out with EDA, DETA, and TETA at 35 °C for 30 min, respectively. Finally, The WPU dispersions with solid content of about 40 wt% were obtained after the acetone was removed.

2.3. Preparation of WPU films

The films were obtained by pouring the WPU dispersions onto a Teflon disk to dry at room temperature for 7 d and then at 50 °C in a vacuum dry oven for 24 h to remove the solvent completely, and then stored in a desiccator to avoid moisture.

2.4. Characterization

The average particle size and distributions of WPU dispersions were measured with a Malvern Nano-ZS laser particle sizer (UK).

The molecular weight of WPU dispersions was measured using a Polymer Laboratories PL-GPC50 gel permeation chromatograph (GPC, UK). All the samples were dissolved in tetrahydrofuran (THF) at a constant concentration 0.1 wt%. The flow rate of THF solvent was 1.0 ml/min and the sample injection volume was 10 μl .

The chemical structure of WPU was analyzed with a Perkin Elmer 2200 Fourier transform infrared spectrophotometer (FTIR, USA).

The crystallinity of WPU film was analyzed by a Bruker D8 advance X-ray diffractometer (XRD, Germany). A scanning of 2θ angle was from 4 to 70°. The scanning speed was 0.1 s/step and the every scanning step was 0.02°.

The dynamic mechanical properties of WPU films were measured at 1 Hz using a Netzsch 242E dynamic mechanical analyzer (DMA, Germany) at a heating rate of 3 °C/min in the temperature range of -100 to 100 °C.

The thermal property of WPU films was measured using a TA Instruments Q20 differential scanning calorimeter analyzer (DSC, USA). 3–8 mg of the WPU films hermetically sealed in an aluminium pan were heated up to 150 °C with a heating rate of 10 °C/min and kept for 3 min to keep a consistent thermal history for the melting process. And then, the samples were cooled to -80 °C at a cool rate of 10 °C/min. The non-isothermal measurement was scanned from -80 to 200 °C with a heating rate of 10 °C/min.

Download English Version:

<https://daneshyari.com/en/article/147231>

Download Persian Version:

<https://daneshyari.com/article/147231>

[Daneshyari.com](https://daneshyari.com)