



Synthesis and characterization of waterborne polyurethane based on aliphatic diamine sulphonate and liquefiable dimethylol propionic acid

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ABSTRACT

In this paper, aliphatic diamine sulphonate (AAS-Na) and liquefiable dimethylol propionic acid (LDMPA) were used together to synthesize waterborne polyurethane (WPU) with excellent property. The influence of $-\text{COOH}/-\text{SO}_3\text{Na}$ molar ratio on the structure and properties of the waterborne polyurethanes were characterized by IR, particle size analysis, DSC, DMA, apparent viscosity, water absorption, contact angle, tensile and peel strength tests. It was found that with decreasing $-\text{COOH}/-\text{SO}_3\text{Na}$ molar ratio from 10:0 to 3:7, (1) the particle size of the waterborne polyurethane emulsion decreased, while the apparent viscosity of the samples increased. (2) the water absorption of the WPU films decreased, while the contact angle of the films increased. (3) The tensile strength, elongation at break and peel strength of the samples increased. Furthermore, the results of DMA showed that incorporation of AAS-Na increased the storage modulus of the sample. And the results of DSC showed that with decreasing $-\text{COOH}/-\text{SO}_3\text{Na}$ molar ratio from 10:0 to 3:7, T_g of soft segment shifted to lower temperature, which indicated that the micro-phase separation degree of the samples increased.

1. Introduction

As increasing demand for reducing volatile organic compounds (VOCs) and hazardous air pollutants emissions, waterborne systems are gradually dominating coating field as a consequence of their lower toxicity compared to solvent-based products. Waterborne polyurethanes (WPU), with good flexibility, environmental friendliness, fire safety and broad substrate suitability, have been widely used in adhesives and coatings for leather, textile, glass, and paper etc. [1–7]. Currently dimethylol propionic acid (DMPA) is commonly used as a hydrophilic anionic chain extender in synthesis of WPU. However, the use of DMPA have several drawbacks, for example, additional organic solvents, such as *N,N*-dimethylformamide (DMF) [8] or *N*-methyl-2-pyrrolidone (NMP) [9–15], are largely demanded to dissolve DMPA. NMP and DMF are characterized as “toxicologically questionable” solvent in European Union, and are very difficult to be completely removed from polyurethane matrix even after distilled in vacuum oven. From the view of environmental and economical consideration, it is very important to avoid using these solvents in the preparation of WPU. In order to overcome this drawback, Ott et al. [16] used *N*-ethyl-2-pyrrolidone (NEP), a low toxic solvent, instead of NMP for preparing waterborne polyurethane. Though its toxicity was lower than NMP, it still showed negative influence on human health. Jasmin et al. [17]

used acetone as solvent instead of NMP. However, it was difficult to be completely removed from WPU. The price of WPU prepared in this method was very high because of the waste and cost of the large amount of acetone. Su et al. [18] and Lee et al. [19] used 2, 2-dimethylolbutyric acid (DMBA) with low melt point instead of DMPA as hydrophilic chain extender to prepare organic solvent-free waterborne polyurethane. However, the price of DMBA was much higher than that of DMPA which limited its application in this field.

In our previous work, WPU based on a liquefiable dimethylol propionic acid (LDMPA) was synthesized without using DMF or NMP in the synthesis process [20], therefore, there was no negative influence on the environment. Unexpectedly, for the existence of LDMPA in the main chain of WPU, the micro-phase separation degree of the WPU samples was decreased, which also decreased the mechanical properties of the samples. A lot of methods have been reported on the way for improving the mechanical properties of WPU, such as increasing the crosslink density and doping inorganic particles et al. [21,22]. However, all these modifications may result in lowering the storage stability of WPU [23–25].

Compared with those that containing carboxyl groups as their hydrophilic groups, WPUs containing sulfonic acid groups have higher solid content, better mechanical, water resistance, acid resistance and alkali resistance properties [26–30]. However, by using sulfonic acid as

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chain extender, during its emulsification process, the chain-extension process can also happen. As a result, the emulsification process is difficult to be controlled. Gelation may be formed during this process which could cause the failure of WPU synthesis procedure [31].

In this paper, aliphatic diamine sulphonate (AAS-Na) and LDMPA were used together to synthesize WPU. The structure and properties of WPU samples were characterized by IR, particle size analysis, apparent viscosity, water absorption tests, contact angle tests, tensile tests, peel strength tests, DSC and DMA. The influence of -COOH/AAS-Na molar ratio on physical properties of WPU was discussed in detail.

2. Experiment

2.1. Materials

Polycaprolactone diol (PCL, $M_n = 3000$) was purchased from Perstor Chemical. Isophorone diisocyanate (IPDI) was purchased from Bayer Chemical. Acetone, Triethylamine (TEA) and Ethylenediamine (EDA) were purchased from Shanghai Heshibi Chemical. Aliphatic diamine sulphonate (AAS-Na) was purchased from USI Corporation. Liquefiable dimethylol propionic acid (LDMPA) was synthesized in the same way as described in our previous work [20].

2.2. Synthesis of WPU

Synthesis of WPU was carried out in a three-neck round-bottom flask equipped with mechanical stirrer, reflux condenser, thermometer, and heating mantle under nitrogen atmosphere. 300.00 g (0.100 mol) PCL 3000, 13.26 g (0.027 mol) LDMPA and 74.60 g (0.336 mol) IPDI were fed into the flask. The reaction was carried out at 80 °C under nitrogen atmosphere for two hours that the theoretical NCO content was reached. The change of NCO content during reaction was determined using a standard dibutylamine back-titration method (ASTM D1638). After the temperature of the polyurethane prepolymer was reduced to 40 °C, Acetone was added to the polyurethane prepolymer to reduce the viscosity of the system. The addition amount of acetone was 20 wt% of the prepolymer. 2.73 g (0.027 mol) TEA was added for neutralizing the carboxyl group of the NCO-terminated polyurethane prepolymer. After neutralization reaction at 40 °C for 30 min, distilled water was added to the reaction mixture under vigorous stirring. The neutralized prepolymer was chain-extended by dropping EDA/AAS-Na (EDA:1.20 g/0.20 mol, AAS-Na:2.28 g/0.012 mol) at 40 °C for 1 h. The aqueous dispersion named LWPU2 (40 wt% solid) was obtained by evaporating acetone. It should be noticed that acetone was used here because we adopted the “acetone method” for synthesizing WPU. All the acetone would be removed by distillation at last. The final product was obtained containing a total hydrophilic group about 10 mmol/100 g. The synthesis procedure is illustrated in Scheme 1. In this manner, four samples with different AAS-Na contents named LWPU1, LWPU2, LWPU3, LWPU4 (COOH/SO₃Na = 10:0, 7:3, 5:5 and 3:7) were prepared respectively. The detailed formula for each sample is listed in Table 1.

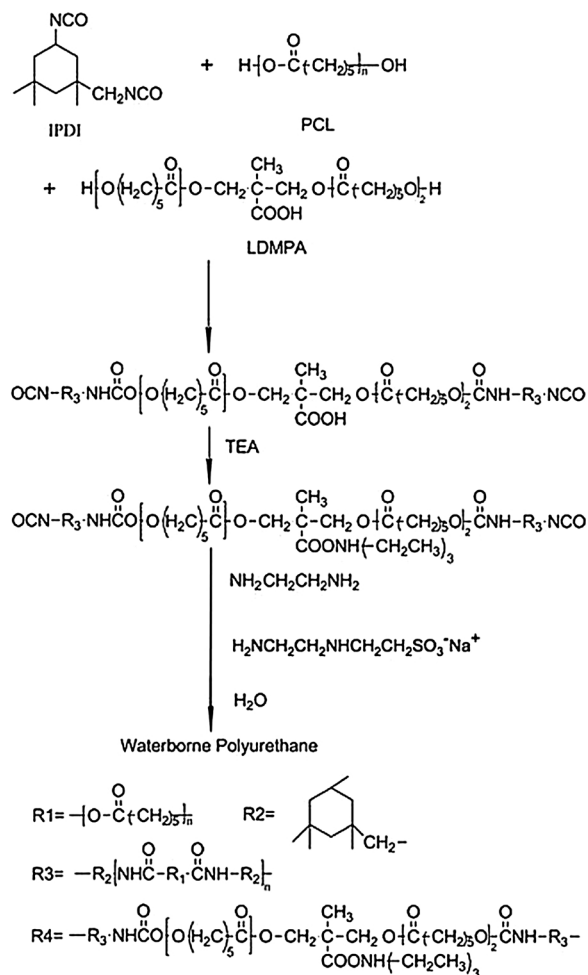
2.3. Characterization

2.3.1. Particle size tests

Particle Size tests were carried out by laser particle size analyzer (Zetasizer Nano ZS, Malvern Instruments Ltd.) at room temperature.

2.3.2. FTIR analysis

The tests were performed on an infrared spectrophotometer (Nicolet 8700, Thermo Nicolet Corporation.) and the spectra were recorded by averaging 64 scans at a resolution of 2 cm⁻¹. The films for infrared analysis were sufficient thin to be within the absorbance range where the Beer-Lambert law was obeyed.



Scheme 1. Synthesis procedure of WPU.

2.3.3. Water absorption tests

First, WPU emulsion was placed on Teflon plate at room temperature for 7 days to prepared related WPU films. Then, the prepared films were cut into pieces with size of 3cm × 1 cm and placed in a vacuum oven at 50 °C for 24 h to remove the residual solvent. The water absorption of the samples was tested by immersing dried sample into distilled water for 24 h. The water absorption rate of samples was calculated according to the following equation:

$$W = \frac{m_t - m_0}{m_0} \times 100\%$$

Where: m_0 is the weight of the dried sample, and m_t , the weight of wet sample.

2.3.4. Tensile tests

Tensile tests were performed on a universal material tensile machine (CMT 6502, Shenzhen Sans testing machine Co., Ltd.) at 25 °C. The size of the samples was 20mm × 5mm × 0.1 mm. The initial length of samples was set to be 10 mm, and the crosshead speed was 150 mm/min. The results were averaged by at least five repeated tests.

2.3.5. DSC tests

DSC data of the samples were obtained on a differential scanning calorimeters (DSC204F1, Netzsch (shanghai) Machinery & Instruments Co., Ltd.) under nitrogen atmosphere with the weight of samples about 8.0 mg. At first, the samples were heated up to 100 °C with a heating rate of 50 °C/min, maintained for 3 min to eliminate the heat history, and then cooled down to -80 °C with a cooling rate of 10 °C/min and maintained for 5 min. Finally, the samples were heated up to 100 °C

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