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Thermal and Crystalline Properties of Waterborne Polyurethane by in situ water reaction process and the potential application as biomaterial

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ABSTRACT

Understanding the role of water in waterborne polyurethane synthesis and properties is a central issue. Water may bring some unique and interesting properties and phenomenon for waterborne polyurethane. This paper focus on the impact of the novel water addition procedure on the properties of waterborne polyurethane. The novel poly(neopentyl glycol adipate) (PNA)-based waterborne polyurethane was prepared using the designed in situ water reaction process. As a comparison, waterborne polyurethane was synthesized through the conventional water addition process through prepolymer method. The thermal and crystalline properties of the obtained polyurethanes were detected by XRD, DSC, DMA, POM, TG and SEM. The results indicated that the novel polyurethane dispersion presents unique performance. Furthermore, to explore the application area of the novel polyurethane dispersion, mold resistance experiments were performed. The result suggested that polyurethane dispersion from the novel process is safer and more environmentally friendly than that from conventional water addition process.

1. Introduction

Waterborne polyurethane (WPU) has sparked much interest in researchers in the past years. Due to the limited effect on the environment and numerous structural features which result in many useful and intriguing properties, such as excellent elasticity, toughness, lustrousness, low-temperature impact property and abrasion resistance, etc. [1,2] It is the only class of polymers that display thermoplastic, elastomeric, and thermoset behavior. It has been widely used as coatings for various fibers, adhesives for alternative substrates, primers for metals, caulking materials, emulsion polymerization media for different monomers, paint additives, defoamers, associate thickeners, pigment pastes and textile dyes [3]. The synthesis routes and methods have been reported in a wide range of studies [4–8], most of them are prepolymer and acetone process to obtain polyurethane prepolymer firstly, and then deionized water is added to emulsify and disperse the hydrophilic WPU prepolymer, with the process of chain extension. However, the polyurethane prepolymer is usually in high viscosity. Thus, it is hard to disperse WPU prepolymer by pumping the prepolymer into deionized water or adding deionized water into the prepolymer. To solve this problem, we propose a novel and environmental method to prepare waterborne polyurethane dispersion, namely system-water generating process. During this process, deionized water is replaced by some kinds of regent which can generate water under controlled conditions.

Two waterborne polyurethane dispersions (PUD), abbreviated as PUD1 and PUD2, were prepared by the novel system-water generating process and conventional deionized water addition process, respectively. In this research, the thermal and crystalline behaviors were studied in detail to analyze the phase separate differences between the two PUD samples. It is well known that polyurethane segmented block copolymers consist of glassy "hard" blocks chemically combined with amorphous (usually isocyanates) and low T_g "soft" blocks (oligomer polyols). The thermodynamic incompatibility between the hard and soft blocks leads to the phase segregation for linear block polyurethanes or polyurethaneureas. All the properties are determined by the phase-separated hard and soft segment. The degree of the phase separate in hard and soft

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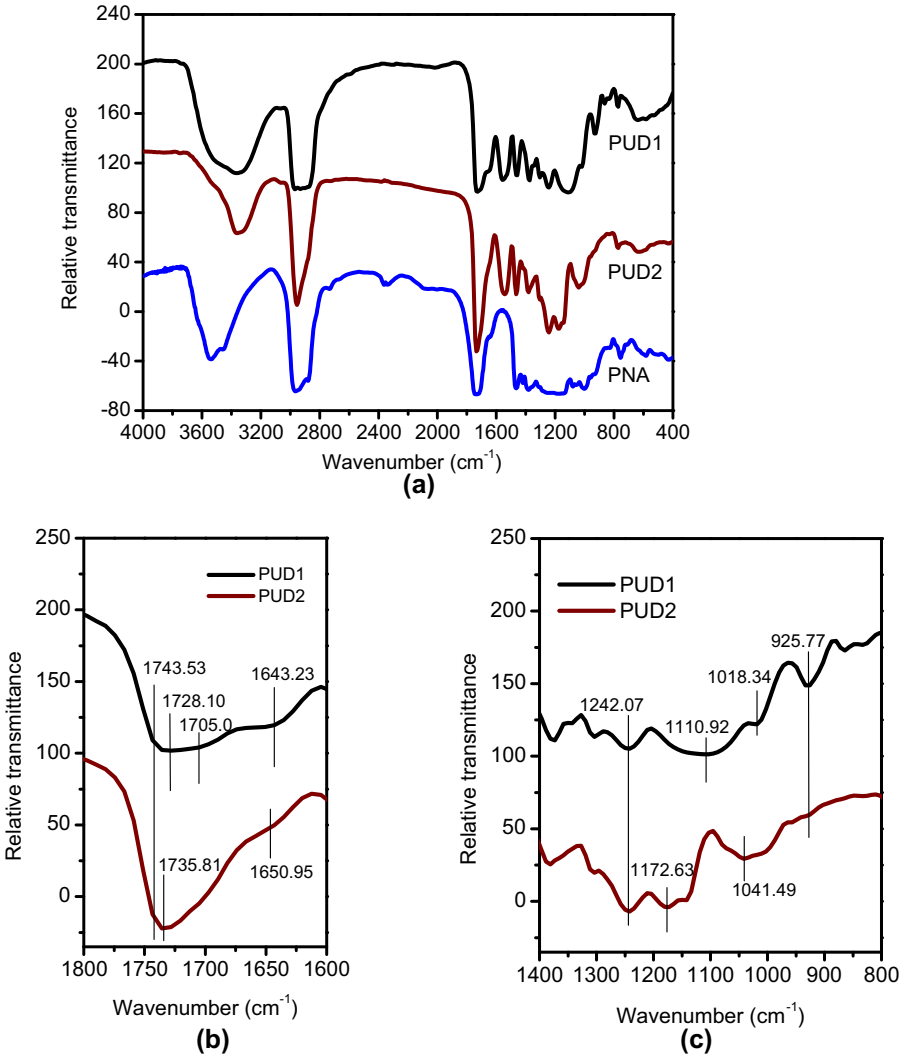

Fig. 1. FTIR spectra of the PNA, PUD1 and PUD2: (a) the whole region from 4000 cm^{-1} to 400 cm^{-1}; (b) the main region for carbonyl group from 1800 cm^{-1} to 1600 cm^{-1} for PUD1 and PUD2; (c) the main region for ether group from 1400 cm^{-1} to 800 cm^{-1} for PUD1 and PUD2.

blocks in microdomains leads to thermodynamic and crystalline differences in polyurethane products, which can be significantly detected by thermal and crystalline experiments. To more fully understand the impact of different water addition process on the polyurethane dispersion properties and phase separation of the PUD1 and PUD2, a series of thermal and crystalline experiments were performed in this research. Moreover, mold resistance of polyurethane dispersions experiments were carried out to explore the potential application as biomaterials.

2. Experiment

2.1. Materials

The diisocyanate used was isophorone diisocyanate (IPDI, 98 wt% purity, purchased from Jingchun Chemical Co., Ltd. Shanghai, China) which is liquid at room temperature. Poly (neopentyl glycol adipate) (PNA, molecular weight (M_w) = ca. 2000) was used as oligomer glycol to synthesize polyurethane samples (dried under vacuum at 120 °C before use). Dimethylolpropionic acid (DMPA) was employed as a hydrophilic chain extender. (purchased from Jingchun Chemical Co., Ltd. Shanghai, China) 1,4-butanediol (BDO, 99.5 wt% purity), and 1-methyl-2-pyrrolidone (NMP, 99 wt% purity) were purchased from Fuchen chemical Co., Ltd. Tianjin, China. H_2O2 (30% water solution, M_w = 34.01, purchased from Tianli Chemical Reagent Co., Ltd. Tianjin, China), potassium hydroxide (KOH, ≥ 85 wt% purity, purchased from Baishi Chemical Co., Ltd. Tianjin, China), Dibutyltin dilaurate (DBTDL) was purchased from Qingxi Chemical Co., Ltd. Shanghai, China. Acetone (AR, purchased from Shuangshuang Chemical Co., Ltd. Yantai, China) was used in little dose throughout the traditional process.

2.2. Synthesis of waterborne polyurethane by deionized water and hydrogen peroxide, respectively

Waterborne polyurethane dispersions (PUD) samples were prepared by adding deionized water or hydrogen peroxide into the polyurethane prepolymer with the hard-/soft-segment molar ratio of 4 and the appropriate NCO/OH ratio of 1.2 [4]. The DMPA content was set to be 5 wt% (with respect to the prepolymer weight) [10]. PNA and IPDI were added to a four-necked flask (500 mL) equipped with a mechanical stirrer, thermometer and spiral condenser in an electric-heated thermostatic water bath. The reaction was carried out at 85 °C for 3 h, then DBTDL was added when the first reaction had occurred for 2 h, followed by the addition of DMPA dispersed in NMP at 60 °C. The reaction was continued at 85 °C for another 2 h. Subsequently, the resulting prepolymer was cooled to about 30 °C, and then BDO with a small amount of acetone was added into