



Chain extension of dimer fatty acid- and sugar-based polyurethanes in aqueous dispersions

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ABSTRACT

The chain extension process of renewable waterborne polyurethane dispersions (WBPUDs) prepared from a dimer fatty acid-based diisocyanate (DDI) and isosorbide (IS), using dimethylolpropionic acid (DMPA) as the internal dispersing agent, was investigated. Ethylene diamine (EDA), adipic dihydrazide (ADH) and water were evaluated as chain extenders. Other variables such as the chain extension temperature, the sequence of addition of the chain extender with respect to the dispersion step and the utilization of a catalyst (triethylamine, TEA) were investigated as well. It was found that EDA extended the NCO-functional prepolymer chains at both 30 and 50 °C, independent of the moment of its addition. A limited extent of chain extension by ADH was observed, which was thought to be caused by the low solubility of ADH in the solvent 2-butanone, used for the prepolymer synthesis. ADH chain extension only took place after removal of the 2-butanone. Water chain extension was observed at temperatures ranging from 50 °C to 70 °C. A good balance was found at 50 °C, where a stable dispersion with a relatively high molecular weight, a small particle size and a narrow particle size distribution were obtained. The usage of TEA during the dispersion process promoted the water chain extension reaction, however, at the cost of dispersion stability. An increased DMPA level has shown to improve the dispersion stability. Dispersion-cast poly(urethane urea) films were found to be thermally stable up to 249 °C (5 wt% mass loss) and had T_g values around room temperature.

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1. Introduction

Polyurethanes offer excellent versatility in terms of their mechanical properties and are widely applied as protective coatings for automotive applications, packaging, textiles and furniture [1–4]. Waterborne polyurethane dispersions (WBPUDs) have been widely used in the coating industry since the 1960s [5–7]. They form a class of latex systems in which organic poly(urethane urea) (PUU)

particles are dispersed in an aqueous medium aided by internal, polymer-bound dispersing agents. Since water is used as the continuous phase instead of organic solvents, WBPUDs have a low VOC (volatile organic compound) content and are environmentally benign. Apart from this, WBPUDs offer high molecular weight poly(urethane urea) polymer particles with low dispersion viscosity, allowing convenient film formation [8–10].

Among alternative dispersion processes such as the prepolymer mixing process [5,8,10], the melt dispersion process [5,8,10] and the ketamine-ketazine process [5,8,10], the ketone-assisted dispersion process [5,8,10] is

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industrially the most widely used process to prepare WBPUDs. Initially, NCO-end capped hydrophobic PU prepolymers are synthesized in the ketone solvent, using a slight excess of diisocyanates in reaction with polyether or polyester polyols and an internal stabilizing agent precursor, mostly dimethylolpropionic acid (DMPA). The neutralization of DMPA is carried out either before (used in this study) or after the prepolymer synthesis by for example a volatile tertiary amine or by an alkali metal hydroxide. In the second step, water is used to disperse the prepolymers solution under vigorous stirring. The resulting prepolymer dispersion is chain extended with diamines, diols or water to obtain high molecular weight PUU products. Finally, the ketone is removed from the dispersions, resulting in a solvent-free PUD system. The urea linkage introduced through the diamine-based chain extension reaction is known to improve the final mechanical properties of the films, such as its modulus and tear strength, by hydrogen-bonding.

In recent years, triggered by the increased oil price and environmental concerns, many biomass-based PUU building blocks, such as lysine-based diisocyanate (LDI), a dimer fatty acid-based diisocyanate (DDI), plant oil-based polyols, sugar-based dianhydrohexitol (DAH) isomers and their corresponding diamines, have become available for the preparation of predominantly renewable-based waterborne PUU coating systems [11–19]. Many studies have been published concerning plant oil-based PUs and PUDs, primarily starting from soybean oil-, linseed oil- and castor oil-derived polyols [20–27] in reaction with conventional, petrochemical-based diisocyanates. Due to their soft and hydrophobic character, the resulting PU products show great potential in applications such as thermoplastic PU elastomers, foams and coatings, with promising impact resistance and water resistance properties [21,27]. However, PU systems from plant oil-based diisocyanates have rarely been reported [24,28], while similar physical properties can be expected, such as chain flexibility and hydrophobicity. Furthermore, the chain extension process of renewable-based PUDs has not yet been given much attention, while some chain extension studies are available related to the petrochemical-based PU dispersions [29–32].

In this work, the preparation and the chain extension of renewable-based polyurethane dispersions has been described. These dispersions contain a fatty acid-based diisocyanate (DDI) and 1,4:3,6-dianhydro-D-sorbitol (isosorbide, IS) as the renewable building blocks, neutralized DMPA (non-renewable) as the internal dispersing agent, and EDA, ADH and/or water as the chain extenders. To optimize the degree of chain extension, several parameters such as the temperature applied during chain extension, the dosing moment of the chain extender with respect to the dispersion step, and the presence or absence of a catalyst (triethylamine (TEA)) were varied. The resulting dispersions were examined with respect to their molecular weight, the particle size and the dispersion stabilization. The thermal stability and the thermal transition temperatures of the dispersion-cast films were studied using TGA and DSC measurements, respectively.

2. Experimental section

2.1. Materials

Fatty acid-based diisocyanate (DDI 1410, 92%, titration value) was kindly supplied by Cognis. Isosorbide (IS, polymer grade, trade name Polysorb® P, 98.5+%) was received as a gift from Roquette Frères. Dimethylol propionic acid (DMPA, 98%), dibutyltin dilaurate (DBTDL, 95%), triethylamine (TEA $\geq 99.5\%$) and ethylene diamine (EDA, 99.0%) were purchased from Aldrich. Adipic dihydrazide (ADH) was kindly supplied by DSM Coating Resins and used without purification. Dry 2-butanone was bought from Acros (>99.5%, Acro-Seal®). Before use, DMPA was dried at 60 °C for 48 h in a vacuum oven. All other chemicals were used as received.

2.2. Preparation of polyurethane dispersions

A typical procedure to prepare PU dispersions includes the NCO-end capped prepolymer synthesis and the subsequent water dispersion process, as shown in Scheme 1. The PU prepolymer synthesis was performed as follows: Isosorbide (IS, 1.02 g, 7.0 mmol) and dimethylol propionic acid (DMPA, 0.71 g, 5.3 mmol) were weighed into a 250 mL round bottom glass flange reactor. Triethylamine (TEA, 0.54 g, for 100% neutralization of DMPA) was injected into the diol mixture to obtain a clear diol solution. Subsequently, dibutyltin dilaurate (DBTDL, 0.56 wt% relative to the total solution) was injected into the diol mixture. While being stirred mechanically, the mixture was heated up to 70 °C using a heating mantle. About 7 mL of 2-butanone was used to dilute the diol mixture. DDI (8.991 g, 14.1 mmol) was then added to this diol solution at 70 °C. Immediately, an additional amount (~6 mL) of 2-butanone was added to dilute the total reaction mixture to a solids content of 50 wt%. Before as well as during the reaction, the reaction setup was continuously flushed with inert gas (N₂) to minimize oxidation and to remove any moisture from the reactor. The reaction was allowed to proceed for 4–6 h, counted from the moment that all the DDI had been added. Subsequently, the NCO content of the resulting PU prepolymer was determined by titration. After the PU prepolymer synthesis, the reaction temperature was decreased to 50 °C and additional solvent was added to correct for solvent loss and to keep the prepolymer concentration around 50 wt%. Approximately 70 mL of de-ionized water was injected in a controlled, continuous way into the prepolymer mixture and the dispersing process was effected by vigorous stirring. Subsequently, the chain extender (CE) EDA was added dropwise during a few minutes to the initially formed dispersion and the chain extension reaction was allowed to run for 1 h. Thereafter, the polymer dispersion was discharged from the reactor. Residual 2-butanone was distilled off at 40 °C under reduced pressure.

3. Characterization

3.1. PU prepolymers and PU dispersions

Size exclusion chromatography (SEC) was used to determine both the molecular weights and molecular

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