



Property profile of poly(urethane urea) dispersions containing dimer fatty acid-, sugar- and amino acid-based building blocks

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ABSTRACT

The understanding of the polymer composition–properties relationship is of great importance to improve the mechanical properties of bio-based polyurethanes containing long chain fatty acid derivatives. In this work, water-borne poly(urethane urea) dispersions containing dimer fatty acid-based diisocyanate (DDI), ethyl ester L-lysine diisocyanate (EELDI), 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS) and dimethylolpropionic acid (DMPA) residues were prepared. The investigation focuses on the thermal and mechanical properties of these dispersion-cast films as well as on the morphology in correlation with the polymer composition. Significant dependencies of these properties and the morphology on the polymer composition are observed. By partially replacing the flexible DDI with the rigid EELDI as well as by increasing the isosorbide contents in the monomer feed, the T_g as measured by DSC was significantly enhanced from 18 to 58 °C (1st T_g) and to above 70 °C (2nd T_g). As evidenced from the DSC, AFM and FT-IR measurements, the H-bonds-induced micro-phase separation was influenced by the polymer composition. The observed improved phase mixing at relatively high EELDI-to-DDI ratio was related to the increased EELDI content and the corresponding urethane/urea bonds. The viscoelastic behavior of these dispersion-cast films showed a strong dependence on the ratio of the flexible DDI to the rigid EELDI and were less dependent on the IS and DMPA contents.

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1. Introduction

Water-borne polyurethane dispersions (PUD) have emerged as important alternatives to their solvent-based counterparts for coating applications due to their reduced volatile organic compound (VOC) contents and the related environmental benefits [1–7]. Their excellent properties such as solvent resistance, impact resistance, film-forming

ability at room temperature and adhesion to many substrates such as wood, textile and metal make them suitable for applications such as foams, coatings and adhesives [4,8–11].

Recently, stimulated by the high, unstable crude oil price and the awareness of the importance of the sustainable development of polymer materials, research in the field of biomass-based polyurethanes (PU) and aqueous PU dispersions has flourished [12–16]. However, restricted by the inherently flexible nature of fatty acid-derived PU building blocks, the corresponding PU materials often exhibit low

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T_g , low strength and poor modulus. By means of cross-linking [17] and designing segmented polymer structures [18–21], the rigidity of the PU materials containing fatty acid derivatives has been significantly improved.

Compared to the chemically cross-linked polymer structure, segmented poly(urethane urea)s (SPUU) have advantageous flexibility to tailor the PU polymers for specific applications [22–27]. The combination of the flexible and rigid chain segments, the type and structure of the building blocks and the presence or absence of physical cross-links (i.e. H-bonds) have shown to influence the polymer properties [23–29]. In aqueous PU dispersions, the segmented polymeric structure has also shown to influence the average particle size and the dispersion stability of the PU dispersions [26–28]. Lee et al. [27] and coworkers have observed a reduction of the average particle size of dispersions by increasing the molecular weight of the soft polyol segments, due to the increased chain flexibility. Therefore, to understand the correlation between the polymer composition, the structure and type of PU building blocks on the one hand and the thermal and mechanical properties of SPUUs on the other, is of great importance.

Preliminary experiments showed that the combination of the flexible dimer fatty acid-based diisocyanate (DDI) (Fig. 1) with the rigid isosorbide (1,4:3,6-dianhydro-D-glucitol, IS) and ethyl ester L-lysine diisocyanate (EELDI), using the non-renewable dimethylolpropionic acid (DMPA) as the internal stabilizing agent and ethylene diamine (EDA) as the chain extender, generated dispersion-cast films with tunable glass transition temperatures (T_g) ranging from 28 to 60 °C. In addition, both IS and EELDI seem to facilitate the dispersion formation due to their relatively high hydrophilicity and the possible hydrolysis of the pendant ester group of EELDI. So far, however, the mechanical properties of dispersion-cast films and their correlation with the polymer composition and the polymer morphology have not been investigated.

This study is aimed at preparing polyurethane dispersions using DDI, DMPA, IS and EELDI as the main PU building blocks, using water (instead of EDA) as the chain extender and TEA as the neutralization agent for DMPA and as the catalyst for water chain extension. The investigation focused on evaluation of the thermal and

mechanical properties of dispersion-cast films as well as the polymer architecture in correlation with the polymer composition. Other coating properties such as the acetone resistance, impact resistance and the adhesion to aluminum were investigated as well.

2. Experimental section

2.1. Materials

Fatty acid-based diisocyanate (DDI[®]1410, 92% pure based on the NCO 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. Ethyl ester lysine diisocyanate (EELDI, 95%) was purchased from Infine Chemicals Co., Limited, China. Dry 2-butanone was bought from Acros (>99.5%, AcroSeal[®]). Dimethylolpropionic acid (DMPA, 98%), dibutyltin dilaurate (DBTDL, 95%) and triethylamine (TEA, ≥99.5%) were purchased from Aldrich. Both diisocyanates and isosorbide were kept under inert gas and in a refrigerator at 4 °C. Before use, DMPA was dried at 60 °C for 48 h in a vacuum oven. Other chemicals were used as received.

2.2. NCO-end capped PU prepolymer synthesis and dispersion preparation

A typical procedure to prepare PU dispersions includes the NCO-terminated prepolymer synthesis in a ketone solvent and the subsequent water dispersion process, as described in our previous work [30,31]. The PU prepolymer synthesis was executed as follows: isosorbide (IS, 1.50 g, 10.3 mmol) and dimethylolpropionic acid (DMPA, 0.64 g, 4.8 mmol) were weighed into a 250 mL round bottom glass flange reactor. Triethylamine (TEA, 0.48 g, 4.8 mmol, for 100% neutralization of DMPA) was injected into the diol mixture to obtain a clear diol solution. Subsequently, dibutyltin dilaurate (DBTDL, concentration: 0.56 wt% relative to the total solution) was injected into the diol mixture. While being stirred mechanically, the mixture was heated to 70 °C using a heating mantle. Approximately half of the total solvent 2-butanone (7 mL) was used to dilute the diol

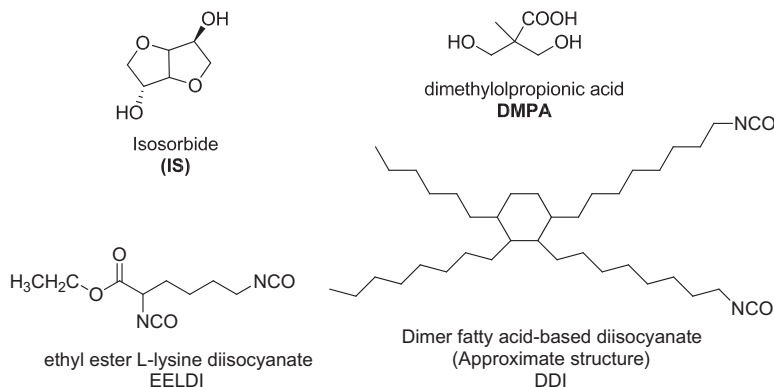


Fig. 1. The structures of DDI, IS, EELDI and DMPA.

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