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Functional properties of films based on novel waterborne polyurethane dispersions prepared without a chain-extension step

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ABSTRACT

A series of novel waterborne polyurethane (PU) dispersions was prepared from a polycarbonate-based macrodiol, 1,6-diisocyanatohexane, 2,2-bis(hydroxymethyl) propionic acid (DMPA) and triethylamine. Different macrodiol-to-DMPA (diol) ratios and different excesses of isocyanate were used, and the typically used chain-extension step was omitted. Systematic measurements of the particle size revealed that PU particles have diameters lower than 100 nm at diol ratios of 1:1 and 1:2, while a diol ratio of 2:1 leads to nanoparticles with diameters closer to 100 nm or higher. The lowest size-dispersity (DLS) index was found for PU dispersions with a diol ratio of 1:1 for all excesses of NCO. The high negative values of ζ-potential (from −40 to −65 mV) of these materials indicate their long-term stability. The tensile properties of flat films made from the PU dispersions depend significantly on the sample composition and vary from 2.7 to 33.8 MPa (Young's modulus), 0.2 to 28.0 MPa (tensile strength), 112 to 1193% (elongation-at-break) and 0.5 to 93.2 mJ mm^{-3} (toughness). The films were found to be thermally stable to a minimum of 200 °C. Dispersions prepared with a 30 and 50 mol% excess of NCO and diol ratios of 1:1 and 1:2 are the most promising materials for practical use as coatings or films. These materials can be used alone or together with water-dispersible additives as the matrix for diverse nanocomposite 2D systems.

1. Introduction

Waterborne polyurethane dispersions (PUDs) are fully reacted, chemically and colloidally stable polyurethane (PU) systems of submicrometre particles. PUDs are a rapidly growing class of polyurethanes that are preferentially used in the production of PU coatings and adhesives for industrial and biomedical applications due to their suitable chemical and mechanical properties and good biocompatibility [1–5]. PUDs are promising materials that meet the requirements of strict environmental legislation and regulations because they produce a low amount of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs), lack harmful monomers and do not release unpleasant odours. In addition, they have superior adhesion and good coating properties for high-performance substrates such as wood, glass, plastics, textiles, rubber, and metal. As a result, the annual global consumption of PUDs reached 267.1 kt in 2011 and is expected to grow to 369 kt in 2018.[1] Currently, the main disadvantage of PUDs is that products made from waterborne PUDs have poor functional (especially mechanical) properties compared to products made from bulk PU analogues. This important problem is primarily solved by the preparation of multicomponent systems, as combining constituents with different properties can lead to materials with functional properties that are suitable and desirable for current practical applications [5–17]. These products are frequently nanocomposites, wherein material reinforcement is due to the presence of inorganic components in the product, such as alkoxysilanes or polyhedral oligomeric silsesquioxanes (POSS) [7–9,13,14,18]. Another possible strategy to achieve PUD-based films with desirable properties is to modify the structure of the prepared PU nanoparticles, leading to systems with relatively simple compositions [19]. A considerable advantage of using novel waterborne PUDs is the possibility of mixing them with water-dispersible nano-additives to prepare PU nanocomposite materials with diverse functional properties.

'Classical' PUDs are based on polyester or polyether diols [20–26]. Despite the wide use of waterborne PUDs, to date, only a few studies have reported the use of polycarbonates (PC) as the soft-segment in prepared PUDs [11,27–33]. However, in all these studies, isophorone diisocyanate was combined with a multifunctional chain extender such as ethylenediamine, diethylenetriamine or hydrazine to give branched

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[1] http://www.transparencymarketresearch.com/polyurethane-dispersions-market.html.

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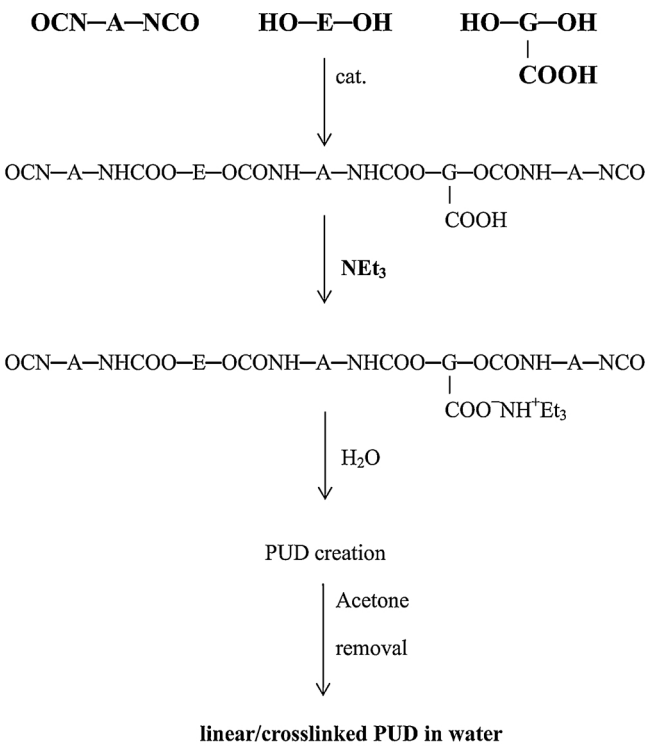

OCN-A-NCO = **HDI** HO-E-OH = **PCD** HO-G(COOH)-OH = **DMPA** NEt_3 = **TEA**

Fig. 1. Schema of waterborne PUD preparation.

or chemically cross-linked polymer structures [27,29–33].

Our recent use of 1,4-butanediol together with a PC-based macrodiol, diisocyanate-1,6-hexane, 2,2-bis(hydroxymethyl) propionic acid and triethylamine resulted in PC-based waterborne PUDs with only physical crosslinking [34]. This procedure is a novel method for the preparation of fully recyclable PU and PU-nanocomposite films [34–36]. Recently, stable PUDs were prepared from identical compounds but without 1,4-butanediol. This modified acetone method of PUD preparation was simplified by eliminating the chain-extension step and using *in situ* water crosslinking (in some cases) [19]. The preparation of novel stable PUDs without the use of a short-chain extender is based on the unique properties of polycarbonate diol, which is used as the main compound in PUD preparation. A slight excess of NCO (1.05 equiv.) in acetone led to the formation of linear rod-like particles, followed by core-shell structures after the addition of water. On the other hand, 1.5× excess isocyanate in acetone led to the formation of either compact spheres or microgel particles. The nanoparticles were initially crosslinked by moisture in the acetone solution, but the final crosslinking took place after the addition of water during the phase-inversion step. PUDs with an average diameter from 42.0 ± 0.6 to 144.2 ± 0.4 nm and a ξ-potential from −40.5 ± 1.8 to −64.9 ± 0.6 mV are mostly stable in water over a long period.

This paper is an extension of the research described in Ref. [19]. In the current contribution, the PUDs were prepared with excess NCO (between 1.05 and 1.5 equiv. per hydroxyl) and were characterized by nanoparticle size, stability and uniformity. However, the main goal of the paper is the detailed characterization of free-standing films prepared from PUDs with different degrees of crosslinking or quantities of cross-linker (given by the excess NCO) and different ionic contents given by soft segment macrodiol-to-carboxylic groups ratio (PC diol-to-DMPA ratio). A series of methods, such as static and dynamic mechanical analyses, DSC, FTIR, TG, SEM, AFM and swelling experiments, were used to characterize the free-standing films.

2. Experimental

2.1. Materials

The aliphatic polycarbonate macrodiol (PCD, trademark T4672), with a number average molar mass (M_n) of ~2770 g mol^{-1} (detected by SEC/GPC), was kindly provided by Asahi Kasei Chemical Corporation, Tokyo, Japan. It is a linear, telechelic oligomer end-capped by hydroxyl groups and consists of butylene (C4) and hexylene (C6) units (molar ratio of C6/C4 = 7:3) connected by carbonate groups. 1,6-Diisocyanatohexane (HDI), 2,2-bis(hydroxymethyl) propionic acid (DMPA), and triethylamine (TEA) were obtained from Sigma-Aldrich Co. Dried acetone (max. 0.0075% H_2O) was supplied by Merck KGaA, Darmstadt, Germany. Dibutyltin dilaurate (DBTDL, purchased from Sigma-Aldrich) was used as a catalyst in the form of a 10 wt% solution in Marcol oil (mixture of liquid saturated hydrocarbons).

2.2. Preparation procedure

2.2.1. Polyurethane water dispersions

PU dispersions were prepared *via* an acetone process without a chain-extension step by varying the PCD-to-DMPA molar ratio in order to control the relative amounts of the soft and hard segments and the ionic content. The ratio $[NCO]/[OH]_{total}$ (where $[OH]_{total} = [OH]_{PCD} + [OH]_{DMPA}$) was varied from 1.05 to 1.5, which corresponds to 5 and 50 mol% excess of isocyanate groups to the total content of reactive hydroxyl groups. The sample codes PUQ x/y:z describe the type and molar ratio of the components. In the codes, Q is either D (waterborne dispersion) or F (free-standing film), x indicates the ratio $[NCO]/[OH]_{total}$, and y:z is the molar ratio of [PCD]:[DMPA]. Series 'PUD x/y:z' refers to the polyurethane water dispersions, and 'PUF x/y:z' refers to the free-standing films prepared from PU dispersions. For simplicity, in this paper, *x* is the 'NCO excess' and *y:z* is the 'diol ratio'. For