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Polyurethane/polyhydroxyurethane hybrid polymers and their applications as adhesive bonding agents

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ABSTRACT

A polyurethane/polyhydroxyurethane (PU/PHU) hybrid polymer was synthesized by reaction of a cyclic-carbonate-terminated prepolymer with triethylenetetramine without employing isocyanates in the final curing step. This cured elastomer contains traditional urethane linkages from the initial prepolymer reaction as well as hydroxyurethane linkages from the final chain extension reaction. The PU/PHU hybrid exhibits microphase separation as made apparent by the presence of two glass transitions and elastomeric properties with Young's modulus of 37 MPa and strain at break of 350%. Most importantly, the PU/PHU hybrid polymer exhibits adhesion to polyimide, poly(vinyl chloride) (PVC), and aluminum substrates that is similar to or enhanced relative to those of polyurethane controls and literature values for typical polyurethane adhesives. In particular, the PU/PHU hybrid has T-peel forces of 7.8, 10.5, and 3.4 N/mm on polyimide, PVC, and aluminum, respectively, and undergoes predominantly cohesive failure rather than adhesive failure. The application of this material as a model consumer-applied adhesive for potential replacement of isocyanate-based polyurethanes is also briefly discussed.

1. Introduction

Polyurethanes (PUs) accounted for 5% of the global polymer market in 2013; 18 million tons of PU are estimated to be produced in 2016 [1,2]. Polyurethanes are typically synthesized from reactions between isocyanates and alcohols. These reactions are often rapid at ambient conditions [3], which allows many PU materials to be field applied by end-use consumers. On the other hand, isocyanates can cause irritation to the eyes, nose and throat and allergic reactions (sensitization) of the lungs and skin [4–6]. Overexposure caused by atomization or heating of isocyanates has been associated with occupational asthma [5]. Engineering controls, use of personal protective equipment, and sound workplace practices enable people to work safely with isocyanates. However, a recent increase in regulatory activity associated with isocyanates [7–10] has created a need to develop chemistries that can reduce or replace isocyanate-based reactions.

Cyclic carbonates are a promising reactant for producing PU-type materials without the use of isocyanates. Multifunctional cyclic carbonate monomers or prepolymers can react with multifunctional amine monomers or prepolymers to produce polyhydroxyurethane (PHU) [2,11–19]; PHUs have received significant attention for their potential as PU replacements. Relative to urethane linkages, hydroxyurethane linkages have some advantages. The hydroxyurethane linkage, which has a secondary or primary alcohol group adjacent to the traditional urethane linkage, allows for hydrogen bonding between carbonyl and hydroxyl groups, thus protecting the urethane linkage from hydrolysis [2]. Relative to PUs, PHUs also tend to exhibit increased chemical resistance, lower permeability, and better thermal stability due to the lack of biuret and allophanate linkages, and lack of porosity because there is no side reaction with water to cause gas formation [12]. However, unlike the typically rapid reaction of isocyanates with alcohols at ambient conditions, the reaction of cyclic carbonates with amines is usually slow at ambient conditions [15]; catalysis has the potential to overcome this issue [18,20,21].

Among the many applications of PUs include use as elastomers and as adhesives. These applications are enabled or aided by microphase separation and hydrogen bonding between urethane linkages. In some cases adhesion is aided by hydrogen bonding between urethane linkages and functional groups on the substrate. To the best of our knowledge, no research has been published in the refereed literature on the production of PU analogs that serve

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as adhesives and that employ cyclic carbonate reactions with amines [22].

Here, we describe the first study to produce PU analogs for use as adhesives in which the reaction of cyclic carbonates with amines plays a key role. In particular, we have designed a hybrid polymer that combines the adhesive properties of traditional PUs with the known and possible benefits of PHUs. As designed, the only reaction that would occur during application by an end-use consumer and subsequent curing would be that of cyclic carbonates with amines; thus, isocyanates would not be present during transport, storage, application or cure of the components used to make the final adhesive. By retaining urethane linkages in the resulting hybrid polymer, we not only retain the known effects of hydrogen bonding [23,24] but also the known abilities of PU to physically adsorb to many substrates via van der Waals interactions and to effectively permeate grooves and pores on substrate surfaces. In addition to the relative advantages of hydroxyurethane linkages over urethane linkages that were described above, hydroxyurethane linkages possess a hydroxyl group which may further enhance adhesion via hydrogen bonding to substrate surfaces that contain appropriate atoms or functional groups.

As designed here, our hybrid PU/PHU polymer is synthesized with a final step involving reaction of a cyclic-carbonate-terminated prepolymer with triethylenetetramine (TETA). The urethane linkages in the hybrid are present in the prepolymer, and the hydroxyurethane linkages are produced in the final curing step from the reaction of cyclic carbonates with amines. We characterize the adhesive properties of the novel PU/PHU hybrid polymer via T-peel strength tests and demonstrate that the hybrid exhibits enhanced adhesion to several substrates as compared to PU controls and literature values for comparable PU adhesives.

2. Experimental

2.1. Materials

Tolylene-2,4-diisocyanate (TDI; SigmaAldrich, 95%) and triethylenetetramine (TETA; SigmaAldrich, 97%) were used as received. Voranol 220-056, a 2000 g mol^{-1} polypropylene glycol polyol (The Dow Chemical Company), was heated to 110 °C in an oil bath under a dry N_2 purge for 12 h to remove residual water. 1,4-Butanediol (SigmaAldrich, 99%), glycerol 1,2-carbonate (TCI America, 90%), glycerol (SigmaAldrich, 99%) and dibutyltin dilaurate (SigmaAldrich, 95%) were placed on active 0.4 nm molecular sieves for 12 h prior to use in order to remove residual water and prevent absorption of atmospheric moisture. Poly(vinyl chloride) (PVC; Tom Thumb Hobby, Midwest Products, Clear 0.38 mm × 193 mm × 279 mm) and polyimide (Kapton Source, 0.125 mm thickness) substrates were used as received. Aluminum substrates (Tom Thumb Hobby, K&S Precision Metals, Aluminum Sheet #255) were ultrasonicated in acetone for 1.5 min and then immersed in boiling deionized water for 30 s to rehydrate the surface. The aluminum substrates were treated less than 30 min prior to adhesive application.

2.2. Synthesis of PU and PU/PHU prepolymers

Materials were synthesized using the prepolymer procedure in Scheme 1. Traditional PU prepolymer was synthesized by reacting excess TDI with dried polyol in a 3-neck round-bottom flask equipped with overhead stirring, a N_2 inlet, and an addition funnel. The polyol (200 g, 0.1 mol) was cooled below 80 °C while under a N_2 purge before being added dropwise to TDI (63.8 g, 0.366 mol) from an addition funnel. The mixture was stirred at room temperature for at least 30 min after polyol addition. Dibutyltin dilaurate was added to the mixture at a loading of 0.05 wt% (0.1319 g, 0.124 mL), and the flask was placed into an oil bath at 80 °C for 2 h.

The procedure described above was also followed to prepare the PU/PHU prepolymer. However, after the prepolymer was stirred at 80 °C for 2 h, a stoichiometric amount of dry glycerol 1,2-carbonate (62.92 g, 0.532 mol) was added. This mixture was stirred for 2 h at 80 °C or until complete disappearance of the isocyanate absorbance peak at ~2200 cm^{-1} [25]. The peak was monitored by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy using a Bruker Tensor 37 FT-IR with a diamond/ZnSe ATR attachment.

2.3. Chain extension of prepolymers

The PU prepolymers were chain extended with 1,4-butanediol or glycerol. The traditional PU prepolymer (15 g, 2.87×10^{-2} mol isocyanate groups) was poured into FlackTek max 20 mixing cups. A 5% loss in isocyanate content was assumed due to possible reactions with atmospheric water during sample preparation and curing. Dibutyltin dilaurate at a loading of 0.05 wt% (0.0075 g, 7 μL) and either 0.014 mol 1,4-butantediol or 9.6×10^{-3} mol glycerol were added to the prepolymer mixture and spun at 3500 rpm for 20 s in a FlackTek DAC 150.1 FVZ-K speed mixer. The mixed materials were placed onto greased Kapton paper and pressed between two aluminum plates at 60 °C and 35 kPa for 1 h; 1 mm or 2 mm spacers were used for pressing. Dumbbell-shaped tensile specimens were cut from the cured plaques using a Dewes-Gumbs die; rectangular pieces for dynamic mechanical analysis were similarly obtained.

The PU/PHU prepolymer (15 g, 3.025×10^{-2} mol cyclic carbonate groups) was poured into FlackTek max 20 mixing cups and chain extended with TETA. The cyclic carbonate concentration was calculated from reagent stoichiometry; no loss of reactive groups was assumed due to the inherent low reactivity and volatility of 5-membered cyclic carbonates. Two PU/PHU hybrid materials were synthesized; the difference regarded the effective functionality assumed for the TETA chain extender. Triethylenetetramine is a linear molecule with four amine groups; a primary amine is located on each of the two chain ends and two secondary amines reside along the backbone. Primary amines react with 5-membered cyclic carbonates more efficiently than internal secondary amines [26]; it was assumed that only some of the secondary amines would react. An effective amine functionality of TETA was taken to be 3.0 or 3.5 (instead of 4.0) and used when calculating the amount of chain extender to add to the prepolymer mix; the ratio of cyclic carbonate to amine functional groups in all materials was 1:1. For the formulation with an assumed TETA functionality of 3.0 (3.5), 0.01 (0.0086) mol of TETA was added to the prepolymer and mixed at 3500 rpm for at least 5 min prior to pressing. A longer mixing time was required for PU/PHU prepolymers due to the increased viscosity of the prepolymer following reaction with glycerol 1,2-carbonate. Samples analogous to the traditional PUs were obtained.

2.4. Preparation of adhesive samples

Adhesive sample preparation was analogous to the procedure outlined above with slight modifications to the substrate setup. According to ASTM D 1876-08 standard test method for peel resistance of adhesives, samples should be peeled for at least 125 mm of their lengths. Thus, 305 mm × 152 mm aluminum plates were used to prepare the adhesive plaques. A polyimide, PVC or aluminum substrate was placed onto an aluminum plate, and 1 mm spacers were arranged onto the substrate so that a uniform material thickness could be obtained. The mixed material was poured onto the substrate, a second substrate was placed on