



Isocyanate terminated castor oil-based polyurethane prepolymer: Synthesis and characterization



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ABSTRACT

The use of new materials from natural origin in the synthesis of urethane-derived polymers is recently drawing eminent care from social, environmental and also economic viewpoints. In this work, NCO-terminated castor oil-based polyurethane prepolymer (COPUP) is synthesized through the reaction between the isophorone diisocyanate (IPDI) and castor oil (CO) with a variable ratio of the isocyanate (–NCO) and hydroxyl (–OH) groups (0.5:1; 1:1; 1.5:1; 2:1) analyzed by nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR) spectroscopy. Furthermore, the polyurethane prepolymers synthesized from IPDI played a significant role of inter-mixing between the soft polyether segments and the hard urethane groups, as shown by the analysis of hydrogen bonding in FT-IR deconvolution. A detailed study of the relationship between structure–property of cured prepolymers was carried out. As a result, COPUP obtained from biomass-derived polyols may enhance a promising alternative to the use of other petrochemicals in the paving industry.

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1. Introduction

Polyurethane (PU) prepolymers are typically isocyanate-tipped macromolecular chains containing urethane groups in their backbone. Prepolymer is a reactive product of polyisocyanates (more than one –NCO) group with at least one other species containing active hydrogen such as polyols (–OH), polyamines, hydroxyl-terminated polyesters, having intramolecular urethane bonds (carbonate ester bond, –NH–COO–) [1,2]. The reaction leads to obtain a unique polyurethane prepolymer composed of polyether or polyester soft segments (SS) and diisocyanate-based hard segments (HS). If the molar ratio of diisocyanate to polyol is above (i.e. 2:1), the resultant product is called a quasi-prepolymers or semi-prepolymer because the diisocyanate molecules partially react with polyol [3,4]. The structural–property relationships in castor oil-based polyurethane prepolymer (COPUP) depends on many factors that include the volume fraction of the hard and

soft segments, the chemical structures and number of the each segment, and as well as the level of cross-linking. These factors influence the physical, chemical, and thermal properties of COPUP and could be manipulated by varying the stoichiometric balance of the components [5]. The polyurethane prepolymers have a different combination rubber-like elasticity along with metal-like toughness [6], durability [7], biocompatibility [7], biodegradability [7] that makes them suitable materials for numerous applications ranging from industrial coatings [8], adhesives [9], and elastomers [12] to biomedical devices [10,11].

Nowadays, the use of vegetable oil is worth being highly taken into consideration because it offers the intrinsic value of reduced toxicity, low cost, high purity and its availability as a renewable agricultural resource [13–15]. In this sense, castor oil (CO) is the only commercially available natural oil polyol produced directly by nature. Due to its high content (around 80 wt%) in ricinoleic acid (12-hydroxy-cis-9-octadecenoic acid) [12]. This fatty acid contains a hydroxyl group at C12 that is, usually, useful for the preparation of polyurethanes without any further modification [16]. As a consequence of the hydrophobic essence of triglycerides, CO provides polyurethanes that have excellent chemical and mechanical properties such as enhanced hydrolytic tendencies, high-tensile strength and elongation, and thermal stability [17].

Based on the above literature this work was to study the synthesis and structure–property relationship of COPUP prepared from

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trifunctional castor oil-based polyols and isophorone diisocyanate. The stoichiometric balance ($-NCO/-OH$ molar ratio) of the hard segment was used to control the final properties of the material. Nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FT-IR), were used to characterize the structure of prepolymers. The physical and thermal properties were studied using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) measurements. The results evidence the adequacy of CO in the synthesis of IPDI-derived polymers, which can constitute a potential candidate for replacing or partially replacing petroleum-based polyurethanes.

2. Experimental

2.1. Materials

The commercial grade of castor oil (CO, $M_n=932$, average hydroxyl functionality of ~ 2.7) was purchased from the local market (BSS grade, Ramcharan Oil mill, Hyderabad). Its characteristic properties of hydroxyl value ($156\text{--}165\text{ mg KOH g}^{-1}$) and an acid value ($1.27\text{--}3\text{ mg KOH g}^{-1}$) were measured according to ASTM standards D1639-89 and D4274-94, respectively. The diisocyanate used was isophorone diisocyanate (IPDI: Z and E isomer in 3:1 ratio, 98 wt% purity), Dibutyltin dilaurate (DBTDL) and Di-n-butyl amine (DBA) procured from Sigma-Aldrich (Milwaukee, WI, USA). Hydrochloric acid (HCL), isopropyl alcohol, toluene, acetone, and ethanol was used as-received from Fisher Scientific Company, Mumbai, India. All reagents were used as received without further purification. Double deionized water (DDI) was used throughout the experiments.

2.2. Synthesis of the NCO-terminated COPUP

The COPUP were synthesized by the reaction between a trifunctional polyol and an excess of diisocyanate (Scheme 1). The synthesis was carried out in a four-necked 500 mL glass flask equipped with a glass stirrer, thermocouple and nitrogen gas inlet. In prepolymer procedure, IPDI flakes were poured into the reactor under a nitrogen atmosphere and heated up to 70°C . The inert atmosphere was used to avoid the ingress of atmospheric moisture and the consequent formation of urea linkages. In a separate vessel, the CO was dried in a vacuum oven at 80°C overnight. When the temperature in the reactor reached 75°C , CO was charged to the IPDI and mechanically stirred with a glass stirrer at 80 RPM. DBTDL was used as a catalyst (0.1 wt% per mol of $-NCO$) so that the reaction could be completed in 2 h. The isocyanate content in the prepolymer during and at the completion of the synthesis was determined by DBA. During the synthesis the changes of absorbance peaks belonging to characteristic functional groups of polyol, IPDI and urethane were monitored by in-line FTIR-ATR spectroscopy. The molar ratio of the hard and soft segment was defined as the ratio ($-NCO/-OH$) between IPDI weight and polyol weight in the starting formulation. The samples were coded as COPUP(0.5:1), COPUP(1:1), COPUP(1.5:1) and COPUP(2:1), where the number behind COPUP represents the content of $-NCO/-OH$ molar ratios, respectively. For Fig. 3: $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) = 0.81 (t, 9H, $-\text{CH}_3$), 1.40 (q, 8H, $-\text{CH}_2$), 2.05 (q, 18H, $-\text{CH}_2$), 2.8 (d, 6H, $-\text{CH}_2-$), 2.92 (t, 6H, $-\text{CH}_2-$), 3.21 (m, 3H, $-\text{CH}-$), 3.56 (s, 2H, $-\text{CH}_2-\text{N}$), 4.10 (p, 3H, $-\text{CH}-\text{O}$), 4.34 (d, 2H, $-\text{CH}_2-\text{O}$), 4.63 (d, 1H, $-\text{NH}-$), 5.21 (t, 1H, $-\text{CH}-\text{O}$), 5.41 (d, 6H, $-\text{HC}=\text{CH}-$). For Fig. 4: $^{13}\text{C NMR}$ (400 MHz, CDCl_3): δ (ppm) = 12.3, 21.1, 23.0, 25.2, 27.0, 29.3, 30.1, 32.5, 33.9, 35.1, 36.2, 37.3, 47.8, 57.1, 62.8, 69.3, 71.4, 75.6, 125.8, 134.1, 156.2, 157.5, 173.26, 207.8.

2.3. Preparation of films

The films were prepared by employing casting technique using stainless steel mold at 25°C . The films were dried at variable temperatures ranging from 40°C , at 60°C and 70°C for 24 h to ensure slow drying for complete in order to remove the solvent. Subsequently, the films were removed from the mold and stored in a desiccator at room temperature for further characterization.

2.4. Determination of NCO content

The $-NCO$ content of the PU prepolymer was determined by the standard DBA back titration. 2–3 g of the prepolymer solution was dissolved in methyl ethyl ketone and mixed with 20 mL of 0.5 molar DBA solutions in toluene. The mixture was left to stand for 30 min, after which isopropyl alcohol (40 mL) was added. Bromophenol blue was used and as an indicator until a color variation from blue to yellow was obtained, the solution was titrated against 1.0 N HCL. Parallel, a blank titration was carried out using the above procedure without any sample.

The $-NCO$ content of the PU prepolymer was calculated according to the following formula:

$$\text{NCO}\% = \frac{(V_b - V_s) \times 42 \times c}{m_s}$$

V_b and V_s represents the volume of HCL consumed in the blank test and titration of the sample, respectively, c is the molar concentration of the HCL, m_s is the mass of the sample, and 42 was the molecular weight of $-NCO$ group.

2.5. Characterization

2.5.1. IR spectroscopy

The FT-IR of the samples was done using Thermo Scientific Nicolet™ 6700 spectrometer in attenuated total reflection infrared (ATR) mode, within the frequency range of $4000\text{--}400\text{ cm}^{-1}$ by co-adding 32 scans and at a resolution of 4 cm^{-1} with strong apodization. Curve-fitting simulations were performed using Origin software. To evaluate and to identify underlying component bands of the N–H and C=O bands were deconvoluted considering peaks as Gaussian with a number of iteration to get the best fit peaks. The maximum error associated with the fit was estimated to be less than 5%.

2.5.2. Nuclear magnetic resonance (^1H and ^{13}C NMR) spectroscopy

The ^1H and ^{13}C NMR spectra of COPUP were recorded in a Bruker Avance-400 MHz spectroscopy by using tetramethylsilane (TMS) as standard at room temperature and samples were dissolved in deuterated chloroform (CDCl_3) as solvent.

2.5.3. Differential scanning calorimetry (DSC)

The DSC was performed on a thermal analyzer (DSC, Q20, M/s TA Instruments, USA). Sample of $\sim 3\text{ mg}$ was heated at a rate of $20^\circ\text{C}/\text{min}$ from -100 to 200°C to determine the glass transition temperature (T_g). The results depicted are taken from the second scan.

2.5.4. Wide-angle X-ray diffraction (WAXD)

The WAXD analysis was performed on a Shimadzu X-ray diffractometer, Japan, (graphite monochromator Cu K α radiation source ($\lambda=0.15406\text{ nm}$) at a scanning rate of $0.5^\circ/\text{min}$ within a range from 1° to 50° . The d was calculated using the Bragg's equation. $\lambda = 2d \sin \theta$.

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