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Thermoplastic Polyurethanes Stemming from Castor Oil: Green Synthesis and Their Application in Wood Bonding

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Abstract: We report an efficient and green approach to synthesize a linear castor oil-based polyurethane (CPU) without using any solvent or catalyst. Diol monomers were first synthesized by the aminolysis reaction between castor oil and diamines; this was accomplished within 6 h at 130 °C. Polymerization of the diols and isocyanate was further confirmed by Fourier transform infrared (FTIR), ^{1}H-nuclear magnetic resonance (^{1}H-NMR), and gel permeation chromatography analyses. The resultant CPUs showed a good thermal stability with an initial degradation temperature higher than 300 °C, and their mechanical and wood bonding property can be modulated by the structures of diamine. In addition, the CPUs possessed a satisfying water resistance property with the water absorption amount lower than 2%. The green conversion of castor oil to thermoplastic polyurethane affords new opportunities in bio-based industries.

Keywords: castor oil; linear polyurethane; catalyst-free; solvent-free

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1. Introduction

The prevalence of polyurethane (PU) has become more frequent since Otto Bayer and his colleagues first introduced it. In order to meet the needs of versatile applications such as elastomers, thermoplastics, thermosets, adhesives, coatings, foams, and fibers [1], the structure of PU should be tailored with various polyisocyanates and polyols. Despite some alternative synthetic routes, including carbon dioxide and monoxide, as well as organic carbonates (e.g., carbonyl diimidazole [2,3] carbamoyl-3-nitro-1,2,4-trizole [4], metal-catalyzed oxidative carbonylation of amines and anilines [5]) have been employed to avoid the application of toxic chemicals, these involving strategies that cannot fully displace the employment of polyisocyanates in industry [6]. Therefore, we should also pay greater attention to seeking renewable polyols and green synthesis methods for PU production [7,8].

Among sustainable resources, vegetable oil is one of the most promising options owing to its inherent renewability, easy modifiability, and relative low cost [8,9]. Vegetable oil, no matter from which source, is generally composed of various triglycerides, the presence of unsaturated bonds making it possible to prepare vegetable oil–based polymeric materials [10–21]. As for the preparation of sustainable PU, different types of vegetable oils, including soybean oil, rapeseed oil, corn oil, palm oil, and sunflower oil, have been exploited as raw materials. Nevertheless, these vegetable oils contain less than two hydroxyl groups per molecule, and their C=C bonds have to be modified via complicated reactions that introduce more hydroxyl groups for PU production. Since involving polyols originating from the oils contain multiple hydroxyl groups, all the resultant PUs are thermosets [22–29]. Among most commercial vegetable oils, castor oil—a non-edible oil naturally containing approximately 2.7 hydroxyl groups per glyceride—has attracted considerable attention for the synthesis of PUs [30–33].

However, thermoplastic PU cannot be produced directly from castor oil because of its multifunctional hydroxyl groups. Up to now, there are very few reports dealing with the synthesis of thermoplastic PU from plant oils [34–36]. Lligadas and co-workers [37–39] utilized the thiol-ene click chemistry method to synthesize a new kind of diol monomer from 10-undecenoic acid, which can be used to prepare linear PUs. Xu et al. [40,41] developed thermoplastic PUs from ricinoleic acid via an approach of transesterification following condensation. Nevertheless, these preparation processes made use of organic solvents and catalysts. The current state of bio-based PU, therefore, encourages us to search for a way to fabricate a bio-based thermoplastic PU without using a catalyst or any organic solvents and that can satisfy the requirements of green manufacturing and engineering.

In the present work, a complete catalyst-free and organic solvent-free method is reported to obtain a linear and double-bond residue castor-based PU. Water resistance and the thermal and mechanical properties of the resultant PUs were investigated using contact angle (CA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and tensile property measurements. Furthermore, the PUs were evaluated as hot melt adhesives for wood-to-wood bonding and showed acceptable adhesive properties.

2. Materials and Methods

2.1. Materials

Castor oil (CO), hexamethanylenediamine (HDA), and ethyldiamine (EDA) with AR grade were obtained from Kelong Chemical Corporation (Chengdu, China) and were used without any further purification. Butanediamine (BDA) was purchased from Aladdin Corporation (Shanghai, China), and hexamethylene diisocyanate (HDI, AR grade) was purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA) and used as received.

2.2. Synthesis of Precursor Diols from Castor Oil

Aminolysis of castor oil was performed in the presence of EDA, BDA, and HDA, and the resultant amide diols were named as EDRA, BDRA, and HDRA, respectively. Typically, castor oil and diamines with a molar ratio of 2:3 were mixed in the reactor under a nitrogen atmosphere with magnetic stirring at 70–130 °C. After reacting for different periods, the reaction mixture was poured into pure water to remove unreacted diamines, castor oil, and the byproduct (glycerol). The solid-liquid mixture was filtered and washed by deionized water three to five times. Finally, the obtained white or buff solid products were toasted by an infrared lamp for 6 h and then dried in vacuum at 50 °C for two days. The sample yields were 85, 88, and 79% for EDA, BDA, and HAD, respectively.

2.3. Preparation of Castor Oil-Based Thermoplastic PUs

Castor oil-based thermoplastic polyurethanes were synthesized via a solvent-free and catalyst-free method at with equal molar ratio of diols to HDI. HDRA (0.03 mol, 24.4 g) was selected as a represent resultant amide diols to react with HDI (0.03 mol, 4.8 mL) as a chain-extender. Typically, HDRA was added into a two-necked flask, which was evacuated and then purged with nitrogen three times. The flask was immersed in a 100 °C silicon oil bath, and the reactant was mechanically stirred after being completely melted. Then, a predetermined amount of HDI was added into the flask. The chain-extension was carried out under continuous stirring for 2 h.

2.4. Characterization Methods

The ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectra of precursor diols and resultant PUs were recorded on a spectrometer (Bruker AC-P 400 MHz, Rheinstetten, Germany) using $CDCl_3$ as the solvent. Gel permeation chromatography (GPC) was performed on a GPC instrument (Waters Co., Victoria, Australia) with a refractive index detector. The samples with a concentration of 2.5 mg/mL were analyzed at 35 °C with tetrahydrofuran as an eluent at a flow rate of 1.0 mL/min. Fourier transform infrared (FTIR) spectra of materials and products were recorded on a Nicolet 6700 spectrometer (Nicolet Instrument Co., Madison, WI, USA). Thermal behaviors were analyzed by a TA Instruments DSC-Q200 (TA Instruments, New Castle, DE, USA). Samples were first heated at 130 °C for 5 min to eliminate their thermal histories and then quenched at −50 °C. After this, the quenched samples were reheated to 130 °C at a heating rate of 10 °C/min. Thermomechanical properties of PU films were measured by a dynamic mechanical analyzer (DMA Q800, TA Instrument, New Castle, DE, USA) in tensile resonant mode with a heating rate of 3 °C/min within −60 to 50 °C. The frequency was fixed at 1 Hz. In order to provide identical samples and to ensure consistency in DMA and tensile test measurements, the synthesized polymers were compression molded by a vulcanizer with a pressure of 10 MPa at 130 °C, and then the obtained films were quenched at room temperature. The PU specimens for DMA analysis were cut into 6×8 mm^2 (width × length) pieces. Tensile properties of the PU films were evaluated by a SANA CMT4104 testing machine (SANS Group, Shenzhen, China) at a crosshead speed of 10 mm/min. The dumbbell shaped specimens with thickness and width of 0.5 and 0.4 mm were used for the measurements, which were carried out at least five times for each sample.

2.5. Wood Bonding and Water-Resistant Testing

Lap shear strength of wood joints were characterized by the SANA CMT4104 testing machine according to the standard GB/T 7124-2008/ISO 4587:2003 [42] Prior to the tests, the teak wood pieces were cut into strips with a thickness of 1.6 mm and 25×300 mm^2 area. PUs were first heated to 100 °C for 5 min and then applied to both pieces of teak wood strips with a thickness of 0.2 mm and a lap joint giving and area of overlap of 25×12.5 mm^2. A load (2.5 kg) was placed over the contact points of wood samples at 25 °C for 48 h. After bonding, each sample was placed at room temperature (25 °C) and 50 ± 5% relative humidity (RH) at least seven times before mechanical testing. The water contact angle was measured by a CA system (Zhongchen Corporation, Beijing, China). Three microliters of deionized water were dropped onto the samples. The PU films were dried in a vacuum oven at 40 °C for 24 h before the swelling experiment. Then, samples were immersed in pure water for more than 24 h to record the weight increments at different predetermined times at room temperature (25 °C). The water adsorption was calculated as the following equation:

$$\text{Water adsorption } (\%) = \frac{W_2 - W_1}{W_1} \times 100\% \tag{1}$$

where W_1 and W_2 represent the initial and final weights of PU.

3. Results and Discussion

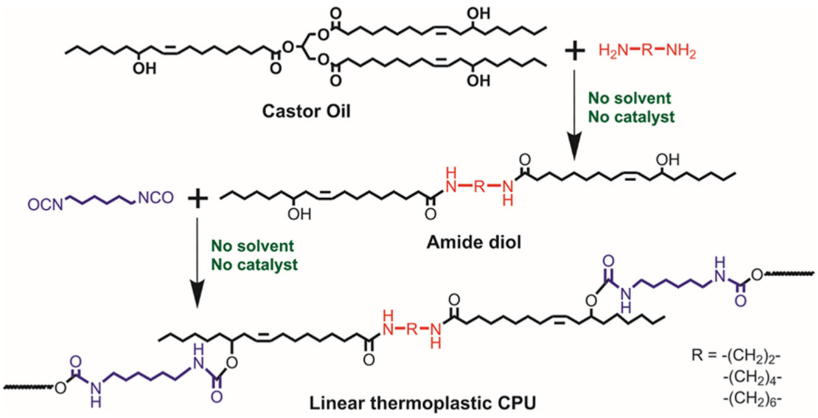
3.1. Synthetisis Procedures

As is well known, castor oil contains approximately three hydroxyl groups and is rarely used to synthesize linear PUs. Therefore, precursor diols are typically obtained prior to the condensation with polyisocyanates. To remove the necessity for a catalyst, in this work, we selected three primary amines (EDA, BDA, and HDA) with high reaction activities to induce the aminolysis of castor oil (Scheme 1). To enhance the "green characteristics" of this approach, water was then applied to remove the unreacted diamine, as well as the product, glycerol. Generally, the reaction temperature and period are two important factors for synthesis of new compounds. HDA, therefore, was selected as a representative diamine to react with castor oil at 70, 100, and 130 °C.

3.2. Structural Characterization

At predetermined reaction time points, the resulting reaction mixtures were characterized by ^{1}H-NMR measurement (Figure 1). The characteristic signals of the castor oil were observed at 3.63 ppm (H_a, –CH), 5.4–5.6 ppm (H_b and H_c, CH=CH), 4.16 ppm, 4.30 ppm, and 5.25 ppm (included in frame I, attributed to glyceride). When HDA was mixed with castor oil, a peak at 3.27 ppm (H_d, –CH$_2$)

was clearly observed. The presence of the signal at 2.70 ppm, from HDA binding to the amine group (the arrow marking in frame II), indicated that the aminolysis reaction was not accomplished within a short time period at a comparably low temperature. With the increase in reaction time at a fixed temperature, the intensity of the peak at 2.70 ppm became weaker and weaker. It should be noted that the peak was not completely absent at reaction temperatures of 70 and 100 °C within 8 h. However, increasing the temperature to 130 °C could remarkably reduce the reaction time: only about 6 h were needed to complete the reaction. Therefore, the aminolysis reactions between castor oil and the other two diamines were also performed at 130 °C, and the ^{1}H-NMR spectra of resultant EDRA and BDRA are shown in Figure 2. As a further investigation of the reaction between CO and diamines, FTIR analysis was conducted to compare the differences in spectra of CO and the resultant amide diols (Supplementary Materials Figure S1). After reacting with different diamines, the absorbance peak of –COOR belonging to castor oil at 1740 cm^{-1} was not detected, and a new peak appeared at 1693 cm^{-1}, which indicated that castor oil could react entirely with the diamines. The results met our expectations and showed that the chain-extension products would be linear thermoplastic polyurethanes.



Scheme 1. Synthetic route to linear castor oil-based polyurethane (CPU).

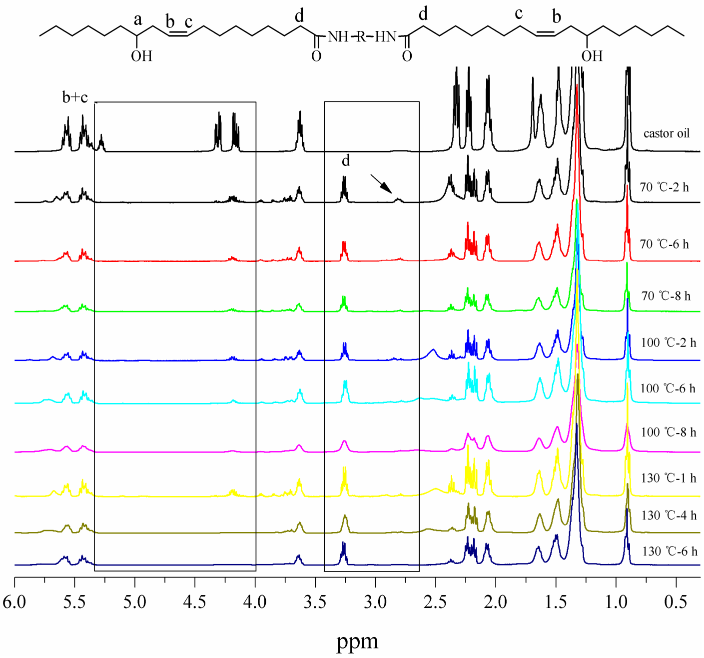


Figure 1. ^{1}H-NMR spectra of castor oil and amide diol monomers synthesized from hexamethanylenediamine (HDA).

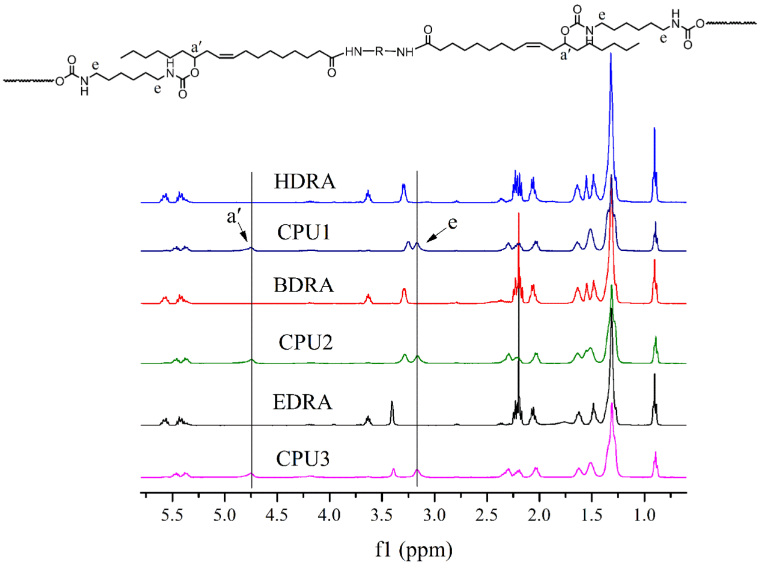


Figure 2. ^{1}H-NMR spectra of EDRA, BDRA, HDRA, as well as their corresponding CPU products.

The secondary OH groups of ricinoleic acid possess a comparably low reaction activity with NCO. Therefore, the reaction temperature was set at 100 °C, which guarantees successful reaction between them. In addition, to prevent a reaction between the secondary NH groups of amide fragment with NCO [43,44], no catalyst was introduced, and the feeding molar ratio of NCO/OH and reaction period were fixed at 1:1 and 2 h, respectively. The resultant PUs based on HDRA, BDRA, and EDRA were named as CPU1, CPU2, and CPU3, and their chemical structures were confirmed by ^{1}H-NMR measurement (shown in Figure 2). The disappearance of the peak at 3.63 (H_a) as well as the appearance of two peaks at 4.75 and 3.16 ppm ($H_{a'}$ and H_e) mean that the polycondensation occurred between HDI and the OH groups of diols. As seen in Supplementary Materials Figure S2, moreover, no absorbance peak was determined between the wavenumbers 2250 to 2270 cm^{-1}. This suggests that there was no NCO group left in the resultant PUs, which is a desirable characteristic for eco-friendly materials. Even though the polymerization was performed in a solvent-free manner, the PDI of resultant CPUs was well controlled at a comparably low level with a M_n of 9.53–11.0 KDa (Table 1). The results indicated that appropriate molecular weights of CPUs were achieved, meeting our expectations.

Table 1. Structure characteristics and mechanical properties of CPUs.

Sample	M_n (kDa)	M_w (kDa)	M_w/M_n	Tensile strength *(TS)* (MPa)	Young's Modulus (MPa)	ε (%)	Lap Shear Strength ($\times 10^5$ N/m^2)
CPU1	9.53	15.7	1.7	6.2 ± 0.2	46.6 ± 3.4	52.0 ± 1.1	12.0 ± 0.2
CPU2	10.9	18.1	1.7	5.0 ± 0.2	43.7 ± 1.9	48.7 ± 1.8	17.2 ± 0.1
CPU3	11.0	20.0	1.8	3.6 ± 0.1	33.2 ± 0.6	69.1 ± 2.5	18.9 ± 0.2

3.3. Thermal Behavior of CPUs

Supplementary Materials Figure S3 shows DSC curves of the CPUs. It shows that CPU1 exhibited no endothermic melting peak, while CPU2 and CPU3 display low-intensity peaks around 60 °C. For HDRA in CPU1, the strong interactions (H-bonds) with the residual urethane groups changed the original conformation and crystallization, resulting in amorphous soft segments in CPU1 and no endothermic melting peak. However, the rest chains of BDRA and EDRA in CPU2 and CPU3 made it difficult to form H-bonds, so the soft segments kept their original conformation and crystal structure. Therefore, small peaks can be observed on the curves for samples CPU2 and CPU3 around 60 °C. Although glassy transition temperatures (T_g) of PUs were observed, it was hard to compute the thermal transition differences from DSC results. To better clarify these differences between the CPUs, DMA measurements were carried out. As shown in Figure 3, all PUs presented similar changes of storage modulus with the increase in temperature. The storage moduli of CPUs were dependent on their structures, that is that CPU1 possessed a higher modulus than the other two CPUs. In addition, only one tan delta peak was found for each PU, and the corresponding T_g increased with a longer length of diamine molecule. The weight ratio of hard segments (the rest of the urethane groups) of CPU1, CPU2, and CPU3 were 17.0%, 17.5%, and 18.1%, respectively. All samples showed similar composition of hard and soft regions. However, urethane groups and amide groups easily form strong interactions (H-bonds). In these cases, longer chain amines might, in fact, lead to greater molecular mobility. It is possible that the more flexible chains of HDA enable the macromolecules to change their conformation in a way that facilitates the formation of strong interactions (H-bonds) with the residual urethane groups. We assumed that all the amide groups in contact with urethane groups form new hard segments. The weight ratio of hard segments was 37.6%, 35.5%, and 33.2% for each CPU, respectively. CPU1 showed a higher hard segment content. In fact, only a part of the amide groups formed H-bonds with urethane groups and thus created a different flexibility of the target molecular. The contents and molecular mobility of diamine chains were the main factors determining flexibility. When the weight ratio of the diamine chain is comparable, longer chains (HDA) more easily move to bond with urethane groups and form H-bonds, which increased the content of hard segments. Thus, a higher content of hard segment of CPU1 resulted in a comparable high mechanical property, as well as a difficult thermal transition [45,46].

Thermal stability of the CPUs is an important factor in application and evaluation by TGA measurement. As shown in Figure 4, 5% of the initial degradation temperatures of all CPUs were higher than 300 °C, which is comparable to some commercialized PUs [47,48], indicating that there were nearly no residues of small molecules in the resultant materials. In addition, a similar one-step degradation method was observed for all CPU samples, indicating that the CPUs possessed a high thermal stability independent of the structure of diamine.

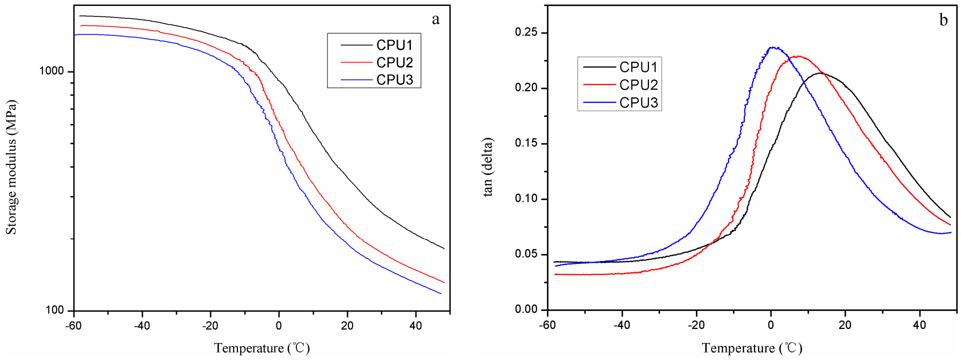


Figure 3. Dependences of storage modulus (**a**) and tan delta (**b**) on temperature for CPUs.

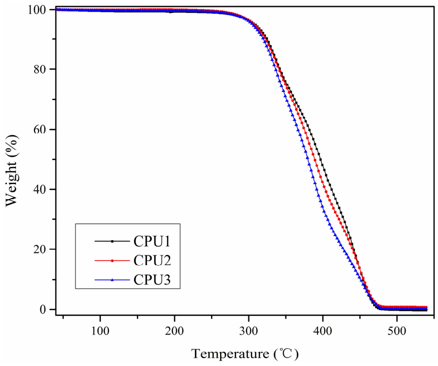


Figure 4. TGA curves of different CPUs.

3.4. Wood Bonding and Water-Resistant Properties

Polyurethane is a class of polymer used as a hot melt adhesive for wood-to-wood bonding. The bonding strength and water-resistance are two very important aspects of adhesive performance of PU. Hence, wood bonding and water-resistant properties of CPUs were studied to find their potential application as bio-based adhesive. Tensile strength (*TS*), elongation at break (ε), and Young's modulus of the CPUs are summarized in Table 1. CPU1 possessed comparably high *TS* and Young's modulus, which were attributed to the higher content of hard segment introduced by strong interactions (H-bonds) between the residual amine groups and urethane groups when using diamine with a longer chain as the aminolysis agent. To further investigate whether the CPUs have the potential to be used as wood adhesives, their wood-to-wood bonding properties were evaluated. As shown in Table 1, lap shear strength of the CPUs was found to be between 12.0 and 18.9 N/m^2, which is comparable to previous reports [49–51]. The lap shear strength increased with the decrease of the chain length in CPUs. This is because higher soft content and lower glass transition temperature (T_g) improve the adhesive properties. This meant that the CPUs synthesized in this work might fulfill the needs of adhesives for wood. Furthermore, the water resistance of adhesive is quite important for practical applications. Water contact angle measurement was utilized to evaluate the surface property of CPU films. As illustrated in Figure 5, the water contact angles of CPU1, CPU2, and CPU3 films were 106 ± 1°, 104 ± 1°, and 97 ± 1°, respectively, showing good anti-wetting properties. In addition, the water uptake amount of the CPU films was suppressed lower than 2%, even after 24-h of immersion, and there were no obvious differences between the samples, which implied a good water resistance of the prepared bio-based PU films.

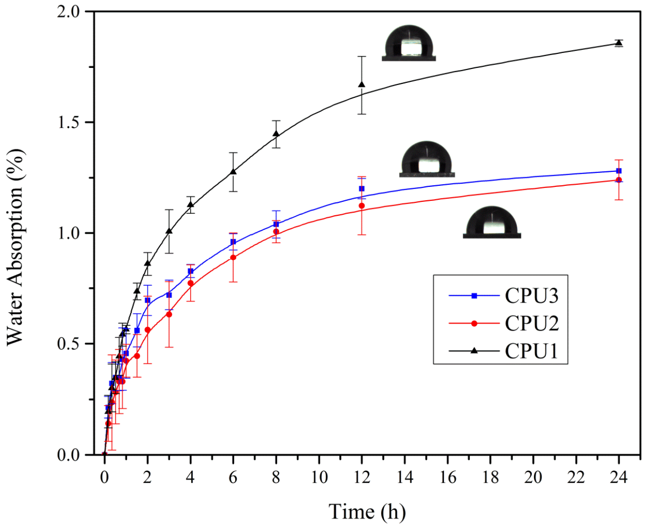


Figure 5. Water adsorption behaviors of CPUs (inserted photos are the illustrations of their water contact angles).

4. Conclusions

A new thermoplastic polyurethane was synthesized from castor oil via a totally catalyst-free and solvent-free procedure under mild conditions. The aminolysis of castor oil with diamines was accomplished completely at 130 °C for 4 h. The CPU synthesized from the diamine with a longer chain length exhibited comparably high tensile strength and Young's modulus. As a wood adhesive, the CPUs met the needs of wood-to-wood bonding and showed outstanding water-resistance, with water adsorption of less than 2%. This means the unique bio-based CPU system reported here shows promise in bio-based adhesive applications. More research needs to be made in our future work to further improve the properties and the range of applications.

Supplementary Materials: The following are available online at www.mdpi.com/2079-6412/7/10/159/s1. Figure S1: FTIR spectra of castor oil and amide diols; Figure S2: FTIR spectra of CPUs; Figure S3: DSC curves of CPUs.

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Author Contributions: Shaolong Li and Changlian Xu conceived and designed the experiments; Changlian Xu performed the experiments; Wenfeng Yang measured and analyzed the ^{1}H-NMR spectra; Qingru Tang measured and analyzed the DMA data; and Shaolong Li wrote the paper. Wenfang Yang and Qingru Tang approved the final version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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