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Doctoral Degree Dissertation

**Development of Biomass-based
Polyurethanes and their Application
as Adhesives**

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By

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Thesis outline

In this thesis, the properties of novel biomass-based polyurethanes were studied and their application as adhesive were developed.

Chapter 1: Introduction

Lignin is one of the most abundant natural carbon resources. The physical and chemical properties of lignin such as surface property, solubility, and molecular weight depend a lot on the extraction processes from lignocellulosic biomass, since their chemical structures undergo dramatic changes after the extraction processes. Therefore, lignin extraction techniques and its applications was briefly introduced in this Chapter.

The chemically stable metabolic intermediate 2-pyrone-4,6-dicarboxylic acid (PDC) can be produced on a large scale from lignin by using transformed bacterium. The main topic of this thesis is the development of PDC-based polyurethanes (PUs). Therefore, the synthesis methods of PDC, the properties of PDC, PDC complexes and PDC-based polymers were explained in detail.

Given the growing trend of replacing petrochemicals with biomass-derived

products, advancing the development of PDC-based functional materials and devices with distinctive and promising features is highly important. Although there are several studies on PDC-based polymers about their fascinating thermal stabilities, mechanical properties, biodegradabilities and adhesive properties, the field of PDC-based polyurethanes (PUs) remains relatively unexplored. This study aims to fill the knowledge gap in PDC-based PU research.

Chapter 2: Materials and General Methods

In Chapter 2, materials and general methods used across Chapter 3 to 5 were explained together for the sake of simplicity. This chapter begins with the detailed information of all the materials used in this research, including the manufacturer and pre-treatment steps, followed by the detailed introduction of all the equipments and characterization techniques used in the following chapters. Finally, the synthesis of bis(ω -hydroxyalkylene) 2-pyranone-4,6- dicarboxylate (BHPDC) was explained here since all the PDC-based PUs involved in this research were started with BHPDC.

Chapter 3: PDC-based Polyurethanes via ROP of δ -Valerolactone

Novel PDC-based PUs were designed and synthesized in this Chapter. The ring-opening polymerizations (ROPs) of BHPDC and δ -valerolactone (δ -VL) were performed in the bulk using an organophosphate, diphenyl phosphate, as the catalyst. The ROPs proceeded in a well-controlled manner even under the

bulk conditions to afford well-defined polyesters with relatively low dispersities. Finally, the one-pot synthesis of PU via the ROP of δ -VL and the subsequent urethane forming reaction was conducted by using the dual catalytic abilities of the organophosphate for both the ROP and PU synthesis. The thermal properties of the PUs were investigated. Self-standing films based on the PUs were fabricated and their mechanical and adhesive properties were evaluated. All PDC-based PUs showed high thermal stabilities, and their melting and crystallization temperatures were found to be adjustable by altering the chain lengths of the PVL segments. The length of these segments also significantly impacted the crystallinity of the PUs, which in turn influenced their mechanical properties. PDCPU50 demonstrated the highest Young's modulus of 212.1 MPa, correlating with its highest crystallinity of 50.5%. The inclusion of PDC units reduced the crystallinity, resulting in softer polymers that were more prone to elastic deformation. Both PDCPU20 and EGPU20 displayed excellent elasticity, exceeding 1500%, indicating that the PDC units did not compromise the inherent mechanical properties of the PUs. Furthermore, PDC-based PUs showed stronger adhesion to metal surfaces (Al, Cu, and Fe) compared to EGPU20, attributed to the 2-pyrone ring-opening addition to the metal surfaces.

Chapter 4: Accelerated Development of PDC-based Polyurethane Adhesives via Machine Learning

In recent years, there has been growing anticipation regarding the application of artificial intelligence (AI) technology across various fields. At the core

of AI lies a technique known as machine learning (ML), which is based on statistical mathematics. In Chapter 4, ML approaches were used to enhance the adhesive properties of PDC-based PUs to accelerate the development of their application as adhesives. The experiments were independently designed and conducted to generate an initial dataset of 25 adhesive samples synthesized from various polyols and isocyanates with different isocyanate-to-hydroxyl ratios (r). Adhesive strengths were measured after hot pressing at different temperatures (T_{heat} , °C) and durations (t_{heat} , h), following a Taguchi L25 orthogonal design. Bayesian optimization (BO) was then applied to maximize the adhesive strength of PDC-based PUs prepared under diverse experimental conditions from a small initial dataset. This approach achieved an impressive adhesive strength of 10.04 ± 1.26 MPa from just 25 initial measurements by iteratively refining the experimental conditions over five BO cycles. Furthermore, these ML models offered valuable insights into optimizing the adhesive properties of PDC-based PUs. Notably, PDC-based PUs synthesized from PEG and MDI with a high isocyanate-to-hydroxyl ratio exhibited strong adhesion when hot-pressed at 200 °C. Although the hot-pressing duration had a marginal effect, longer durations still contributed to enhanced adhesive strength. Achieving strong adhesion needs to balance the ring-opening temperature of the 2-pyrone ring in PDC with the decomposition temperature of PDC-based PUs. Finally, the dataset after BO was trained using regression models for predictions. Among five regression models, Random Forest showed the best performance.

Chapter 5: Tailoring Rapid-Adhesion Properties of Polyurethanes Synthesized from PEG, MDI, and Biomass-Derived PDC

In Chapter 5, BHPDC, MDI, and PEG with different molecular weights were used to synthesize novel PUs aimed at achieving strong adhesion in a short time to reduce the cost for industry application of PDC-based PUs, based on the results from Chapter 4.

First, the adhesive properties of PDC-based PU synthesized from PEG2000 and MDI with an isocyanate-to-hydroxyl ratio of 6 were evaluated under various heating times at 250°C. The results indicate that shorter heating times at higher temperatures generally yield better adhesive strengths, likely due to reduced thermal degradation. Notably, the highest measured adhesive strength (6.68 MPa) was achieved with a heating time of 0.5 h. These findings demonstrated the potential for achieving optimal adhesive properties at elevated temperatures within shorter heating durations.

Subsequently, the adhesive properties of PDC-based PU (PEG2000, MDI, $r = 6$) were evaluated across refined heating temperatures with a constant heating time of 1 hour. The results indicate that a heating temperature of 225°C yields the highest adhesive strength (9.60 MPa). This optimal condition highlights the importance of refining heating parameters to maximize adhesive performance. In contrast, lower temperatures, such as 175°C, result in significantly reduced adhesive strength (3.42 MPa), indicating insufficient thermal energy for effective 2-pyrone ring-opening and subsequent adhesive bond formation.

Finally, two novel PDC-based PUs were synthesized from PEG6000 and MDI with different isocyanate-to-hydroxyl ratios of 6 and 10. This change in molecular weight aims to address the handling difficulties associated with PEG2000-based PUs. The results revealed that while the higher molecular weight improves mechanical properties, it may reduce the overall adhesive strength due to a lower ratio of PDC units. The highest adhesive strength (9.79 MPa) was achieved at 225°C for 1 hour, indicating that a higher isocyanate-to-hydroxyl ratio of 10, combined with elevated temperatures, yields optimal adhesion. This confirms the crucial roles of PDC units in improving adhesion, as increasing the PDC unit ratio can counteract the adverse effects of longer PEG chain lengths on adhesive strength. Notably, optimal conditions are specific to the isocyanate-to-hydroxyl ratio and the molecular weight of the polyol used, as the interactions between thermal energy input, polymer structures, and thermal degradation are complex and require precise optimization.

Chapter 6: Conclusion and Future Prospects

In Chapter 6, the results and discussion from Chapter 3 to 5 were concluded. PDC-based polymers are promising materials not only for serving as alternatives to petroleum-based materials but also for their fascinating properties. Future research should aim to refine predictive models by adding new data points to fill the gap, explore broader experimental conditions including the searching range of experimental conditions and the selection of chemical structures, and extend the applicability of these findings to different substrates and industrial applications. Given the considerable attention attached to the utilization of

biomass materials, PDC-based polymers are expected to be applied in more fields as high-performance and green materials.