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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary (approx.800 English Words)

In Chapter 1, as for lignin, one of the most abundant natural carbon resources, its extraction techniques and applications were briefly introduced. 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 dissertation 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.

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.

In Chapter 3, novel PDC-based PUs were designed and synthesized. 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 polyvalerolactone (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.

In Chapter 4, machine learning (ML) approaches were used to enhance the adhesive properties of PDC-based PUs and 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.

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. The adhesion properties of these PDC-based PUs were investigated under different heating conditions. For PUs synthesized from PEG2000 and MDI with an isocyanate-to-hydroxyl ratio of 6, optimal adhesive property (9.60 MPa) was obtained at 225° C for 1 h. Additionally, while the higher molecular weight of polyol improves mechanical properties, it may reduce the overall adhesive strength due to a lower ratio of PDC units in the polymer. PUs synthesized from PEG6000 and MDI with a higher isocyanate-to-hydroxyl ratio ($r = 10$) exhibited improved adhesion (9.79 MPa) at 225° C, demonstrating the crucial role of PDC units in enhancing adhesive performance.

In Chapter 6, the results and discussion from Chapters 3 to 5 were concluded. The future of PDC-based polymers, which are expected to be used in more fields as high-performance and green materials, was proposed.