Lignin based materials with intrinsic recyclability

Impact

Global warming and environmental pollution caused by the consumption of fossil resources in production activities have become increasingly prominent issues of social concern. Traditional economic model, which primarily relies on fossil raw materials, is no longer suitable for the development requirements of the new era. In the future, major economies will adopt green, and resource-recycling principles to achieve low-carbon, and sustainable development goals. Therefore, the development and utilization of biomass resources to replace fossil resources has attractive prospects. According to a recent report [1], the production capacity of biobased polymers worldwide was 4.4 million tons in 2023 and is expected to increase to 10.5 million tons by 2028, with a compound annual growth rate (CAGR) of approximately 17%. This is significantly higher than the average growth of fossil-based polymers (3-4%). To date, only a small scale of biobased materials have been commercialized for the thermoset market. For instance, epoxidized plant oils has been offered as epoxy resins based on natural and non-toxic precursors. However, the low reactivity of the internal epoxy groups along their aliphatic backbone and the low glass transition temperatures (T_g) resulting from the alkyl chains limit their competitiveness against bisphenol A (BPA)-based materials with high T_g and modulus. Natural aromatic materials, lignin, can reinforce plant tissues through the rigid aromatic rings. Nevertheless, the utilization of lignin remains low, less than 5%. The massive potential of lignin is still undervalued.

In addition to the challenge of replacing fossil-based materials with biomass materials, the disposal and recycling of thermoset materials remain significant obstacles, as these materials persist long after their useful life has ended. Consequently, landfill and incineration remain the primary methods of disposal. In response to this issue, the development of new materials has become increasingly urgent. Covalent adaptable networks (CANs) have been proposed as a solution to thermoset recycling by leveraging reversible bonding.

The main objective of this thesis was the development of lignin based covalent adaptable networks (CANs). There are two major challenges in this study. The first is the modification of the required reactive groups on soda lignin. In particular, lignin can undergo a self-polymerization during the modification, resulting in an increase in the molecular weight, a decrease in solubility and functionality of lignin. In addition, the characterization of CANs also faces challenges. The crosslinked CANs do not dissolve or melt just like a thermosetting material. Therefore, it is difficult to quantitatively study the formation of networks. The above challenges have been systematically solved. Modifications of lignin are achieved through transesterification (Chapter 2) and acetalization (Chapter 3). The transesterification was conducted at

130°C without a catalyst, while the acetalization was conducted at 80°C. The molecular weight of the modified lignin increases slightly as a result of the modification, but its dispersion and thermal stability remain unchanged. This indicates that the modified lignin maintains its stability throughout the modification process. In addition to using modified lignin, we also directly utilized unmodified lignin in CAN materials, demonstrating the direct application potential of lignin (Chapter 4). The crosslinking density can be derived from the modulus of the rubbery platform in the DMA test. The macroscopic evidence of the dynamic exchange of the material is obtained from recycling of the CANs. The microscopic view of the dynamic exchange process is obtained through the rheological characterization (stress relaxation) of the material. CANs often struggle to balance creep resistance and reprocessability. Typically, the more active the dynamic chemical bonds within CANs, the better the reprocessability, yet it tends to compromise the creep resistance. Incorporating lignin can mitigate the flowability of CANs through the introduction of a hyperbranched topology, thereby enhancing the creep resistance. This aspect has been extensively discussed in Chapters 2 to 4. Furthermore, this thesis explores the enhancement of lignin-based CANs by constructing a dual-network system in Chapters 6 and 7 (CANs + hydrogen bonds, CANs + crystalline material). The results demonstrate that the common dual-network system is equally applicable to CANs.

In addition to introducing the prepared recyclable lignin-based CANs, we also conducted a preliminary exploration of its potential applications. Structural adhesives are crucial for constructing lightweight structures in major industries such as construction, and the automotive sector. Epoxy thermosets are considered as one of the most important structural adhesive categories due to their inherent strength and stability, and have immense potential in adhesive manufacturing and service. However, disposal of these adhesives at the end of their life cycle would pose significant challenges, particularly in cases where the substrate needs to be recycled. Separating multilayer structures without damaging the bonded substrates while maintaining good properties during the use phase would be highly desirable for construction applications. Based on the above needs, we have successfully prepared high-strength on-demand adhesives. Adhesives can be debonded at elevated temperatures (in Chapter 2, 4 and 6). Next to adhesive applications, coating applications were also studied. During the use phase of coatings, it is important to note that regular inspection and maintenance are required to ensure the longevity and efficacy of coatings. Typically, coatings may require reapplication in cases of damage, leading to incompatibility issues between the new and original coatings, resulting in delamination, cracking and reduced stability compared to the original coating. Although complete removal and reapplication of the original coating could address this problem, the difficulty of removing the existing coating poses challenges, making the process complex and inefficient. In this study,

we have developed lignin-based coatings that use imine crosslinks, which can enable localized material repair through selective heating after damage. In scenarios with larger damaged areas, additional coating material can be introduced and repaired through heating, forming a strong bond via intermolecular exchange, thus avoiding incompatible interfaces between the new and old coatings. When the coating is no longer viable for repair, it can be easily removed using solvents, enabling the recycling of substrates (in Chapter 3). In addition to conventional applications in adhesives and coatings, lignin-based CANs are expected to play a role in photothermal conversion materials in Chapter 6 and shape memory materials in Chapter 7. Advanced applications give lignin-based CANs the possibility of high benefit.

Finally, we once again highlight that the goal of the circular economy is to maximize resource utilization and reduce waste. By combining the ideas of biomass resources and CANs, we create recyclable materials that not only reduce the use of petroleum-based materials, promote the green transformation, but also reduce waste production from a recycling perspective.

[1] P. Skoczinski, M. Carus, G. Tweddle, P. Ruiz, N. Hark, A. Zhang, D.d. Guzman, J. Ravenstijn, H. Käb, A. Raschka, Bio-based Building Blocks and Polymers – Global Capacities, Production and Trends 2023-2028, 2024.