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Plant-derived thermoset: furan resin and its curing control

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Furan resin is a plant-derived thermoset resin, based on a furfuryl alcohol monomer synthesized from xylan, a part of hemicellulose. Since alternative bio-plastics replacing petroleum products have been explored to solve recent environmental issues, furan resin is highly considered as one of the candidates that promotes a sustainable society. Furan resin is known for its acid-catalyzed curing mechanism, which has not yet been completely reviewed. Because of its rigid 3D crosslinks, cured furan resin is advantageous for chemical resistance, heat resistance and weatherability. On the other hand, its brittleness and difficulty on its curing design limits its application. In this study, the two different aspects of furan resin were investigated as follows: (i) the activation of furan resin curing by oxygen, (ii) curing control of furan resin using the acid trapping function of alicyclic epoxy resins.

The five chapters constitute this thesis.

Chapter 1 outlines the research background and the potentiality of furan resin as an alternative resin to petroleum resin. It was previously found that furan resin has a brittle mechanical strength and complicated mechanism of curing, which is essential to solve in order to replace petroleum resin products. To achieve that improvement, oxygen's effect on furan resin curing and its unrevealed mechanism should be pursued. Besides, a more controlled curing system is required to shorten the curing schedule to prevent bubbling.

Chapter 2 describes the activation of furan resin curing by oxygen. Based on the chemical analyses, oxygen was found to promote furfuryl alcohol polymerization qualitatively and quantitatively, suggesting the activated formation of not only chain extension but also the formation of the precursor for 3D crosslinking. Meanwhile, it is thought that the addition of hydrogen peroxide as an additional oxygen resource enhanced the glass transition temperature (Tg), and simultaneously induced the deformation of the furan rings.

In Chapter 3, since it is believed that cycloaliphatic epoxy functions as an acid scavenger, the control of acid curing agent, namely p-toluene sulfonic acid (TsOH), by addition of epoxied cyclohexene into furan resin was attempted. Firstly, the attempted cycloaliphatic epoxies succeeded on the control of exothermic temperature of furan resin curing. Secondly, the curing schedule was built up based on the DSC isothermal and TGA, and successfully achieved even shorter curing time as well as cured furan resin with no void,

compared to the conventional curing system where the volatilization step and curing reaction step occurs at the same time. This is because the cycloaliphatic epoxy-furan resin hybrid cure successfully separated these steps. In addition, this renewable curing system also achieved higher mechanical property and Tg, while FT-IR shows the possibility of further 3D crosslinks by postcuring at 180 ^{o}C for 1h.

In Chapter 4, because the cycloaliphatic epoxies tested in Chapter 3 are produced from petroleum resources, limonene oxide, plant-derived cycloaliphatic epoxy, was also investigated to accomplish the curing control maintaining the sustainability of furan resin. Although limonene oxide showed weaker scavenging of TsOH due to its methyl group neighboring the epoxy group, the temperature control of furan resin's exothermic behavior was attained. The curing control by limonene oxide resulted in the shorter curing time, the same as in Chapter 3, and vulnerable mechanical properties. Hence, the multifunctional limonene oxides were expected for higher mechanical property. The multifunctional limonene oxides showed the same controllability of furan resin thermoset and short curing time as limonene oxide, confirmed by DSC. The mechanical properties were superior to limonene oxide as expected, and remarkably, the tetrafunctional limonene oxide (TEL) accomplished the highest mechanical property and Tg. As a conclusion, the furan resin-multifunctional limonene oxide curing system successfully achieved the controllability of furan resin thermoset, and showed high mechanical strength in order to be a sustainable substitute.

Chapter 5 summerized the entire discussion.