Renewable Furfural-Based Sulfur-Bridged Epoxy Resins with Excellent Adhesive Properties

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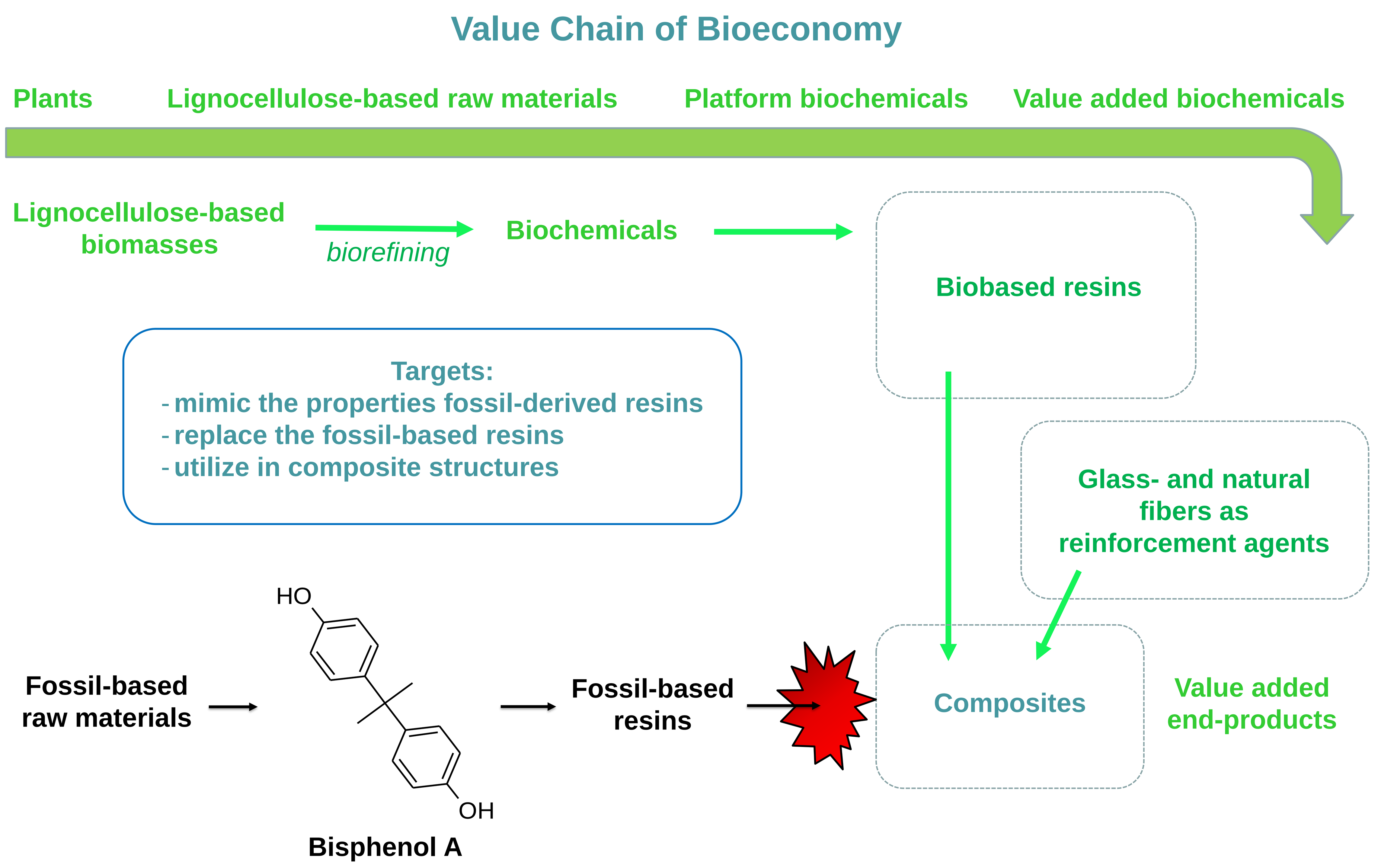
General idea for the FurBio research



Introduction

Current thermoset systems rely heavily on fossil-based resins and hardeners, with their consumption continuously increasing. Notably, diglycidyl ether of bisphenol A (DGEBA) is the primary component of commercial epoxy resins, despite the well-documented health hazards associated with bisphenol A (BPA).

In this work, we synthesized two novel biobased epoxy resins that exhibit material properties comparable to, or better than, those of fossil-based DGEBA.

These resins can be manufactured from commercially available furfural, a hemicellulose-derived compound that can be produced from industrial and agricultural lignocellulosic residues.

Furfural is a particularly promising platform chemical due to its lower production cost compared to the widely studied 5-hydroxymethylfurfural (HMF).

Increasing the production of bioplastics contributes positively to climate mitigation by reducing CO_2 emissions and helping to limit the rise in global mean temperature.

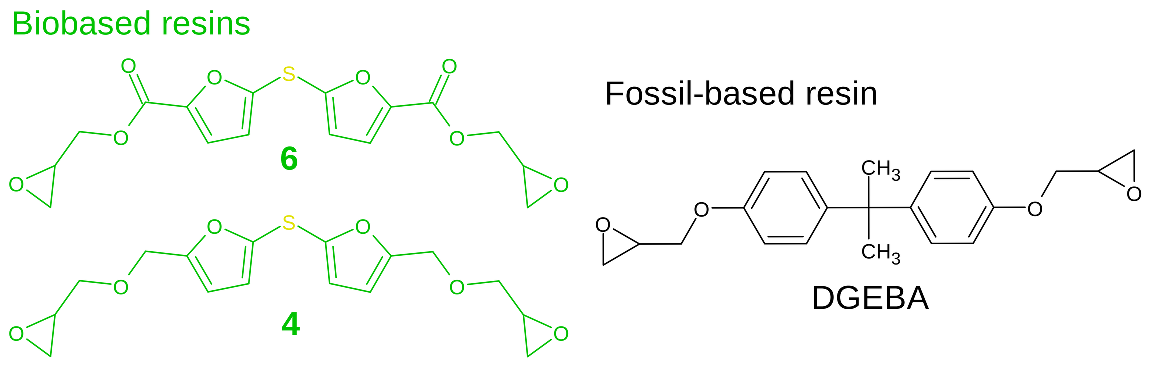
Materials and Methods

Novel biobased epoxy resins were successfully synthesized with high yield and purity. Their structures and purities were confirmed using NMR spectroscopy, high-resolution mass spectrometry, and epoxy equivalent weight titration.

The resins were cured with methylhexahydrophthalic anhydride, using optimized amounts of 2-ethyl-4-methylimidazole as the initiator.

A comprehensive evaluation of the resins was conducted, including their curing behavior, thermomechanical properties, thermal stability, water absorption, tensile strength, and adhesion performance.

The carbon content in these bioresins can be entirely derived from lignocellulose-based biomass, as all carbon-containing starting materials are obtainable from renewable sources.

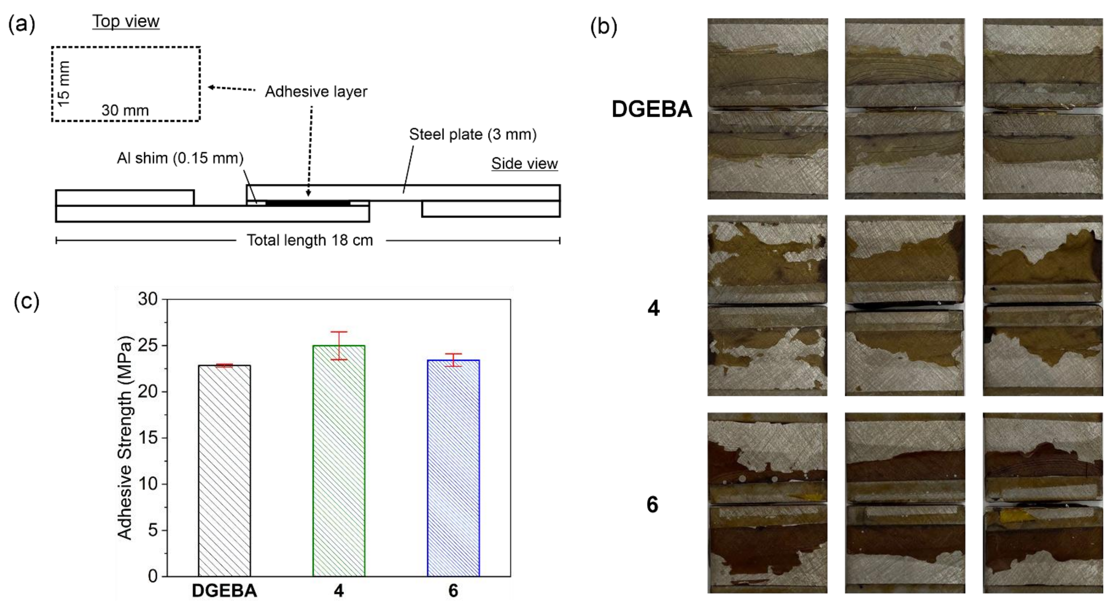


Results

Mechanical analysis revealed that the cured bioresins exhibit superior tensile strength compared to conventional DGEBA-based resins.

Resin	Tensile Strength (MPa)	Elongation at Break (%)
DGEBA	45.1 ± 3	5.4 ± 0.6
4	64.1 ± 3	6.6 ± 0.4
6	57.8 ± 4	7.4 ± 2

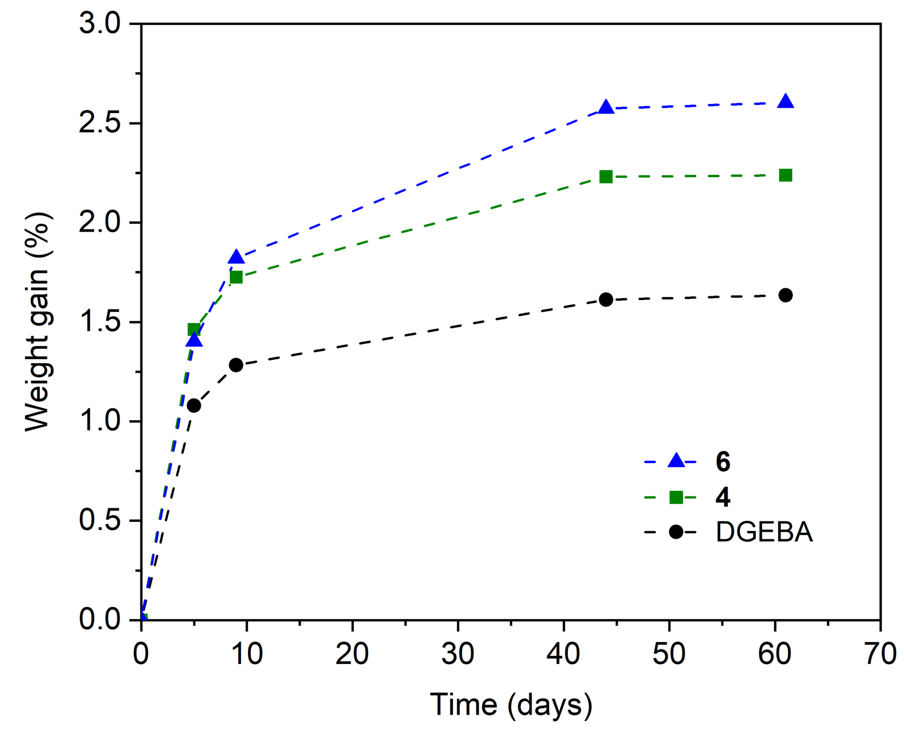
A similar trend was observed in single-lap joint adhesion tensile tests, consistent with the mechanical tests of the plain resins.
Thick metal plates were glued together using a thin layer of resin as the adhesive.



Each of the cured epoxy systems showed good thermal stability.

Resin	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	$T_{d50\%}$ (°C)	R_{700} (%)
DGEBA	350	365	407	11.7
4	279	291	375	22.2
6	298	324	360	9.2

As expected, the cured bioresins exhibited slightly higher water absorption due to hydrogen bonding associated with hydroxyl groups.



Conclusions

The synthesized bioresins demonstrate significant potential as alternatives to DGEBA in various applications, with the added benefit of lowering associated environmental and health hazards.

Reference: Terho, R. A; Kainulainen, T. P.; Salonen, M. A.; Sirviö, J. A.; Heiskanen, J. P. Renewable Furfural-Based Sulfur-Bridged Epoxy Resins with Excellent Adhesive Properties. Macromolecules 2024, 57, 10735−10744. DOI: 10.1021/acs.macromol.4c01000

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