Sustainable rubber composite materials by dynamic covalent networks and bio-fillers

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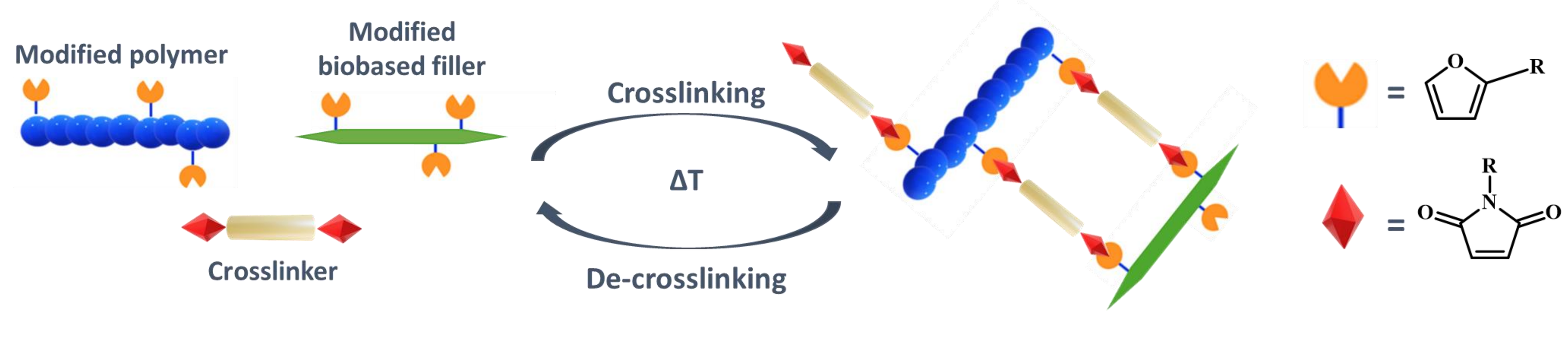
Introduction

Liquid polybutadienes (LPBDs) are low-molecular-weight, unsaturated oligomers in liquid form that offer numerous advantages in processing, performance, and environmental impact across a range of rubber and elastomer applications. However, conventional LPBDs undergo irreversible curing, resulting in non-recyclable waste at the end of their lifecycle. To enhance their properties and stability, reinforcing fillers are typically incorporated into LPBD-based rubber composites. Improving the sustainability of these elastomeric materials can be pursued through two main approaches: modifying elastomers to enable **reversible crosslinking**[1,2] and developing **fillers derived from biomass.**[3]

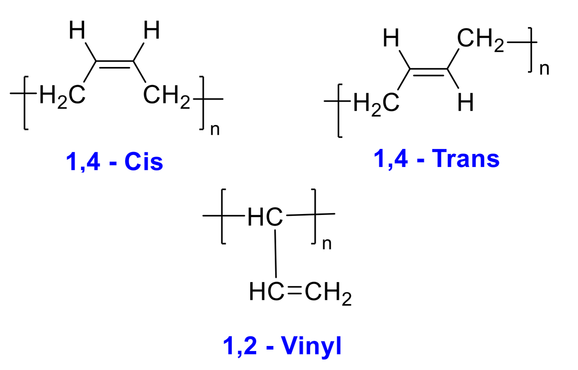
As part of the **MadABio project**, this study focuses on modifying LPBDs and cellulosic bio-fillers to create **renewable, recyclable, and reprocessable composites** based on dynamic covalent Diels–Alder networks.

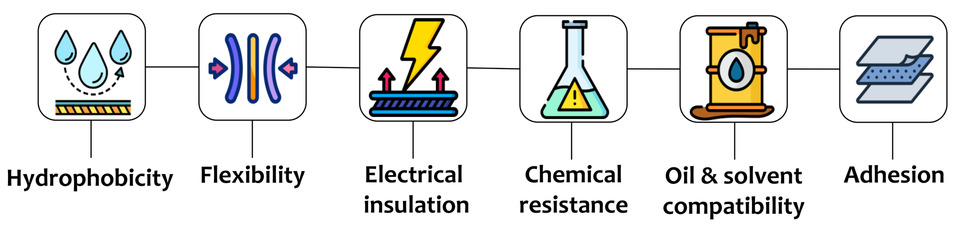


Diels–Alder reversible chemistry

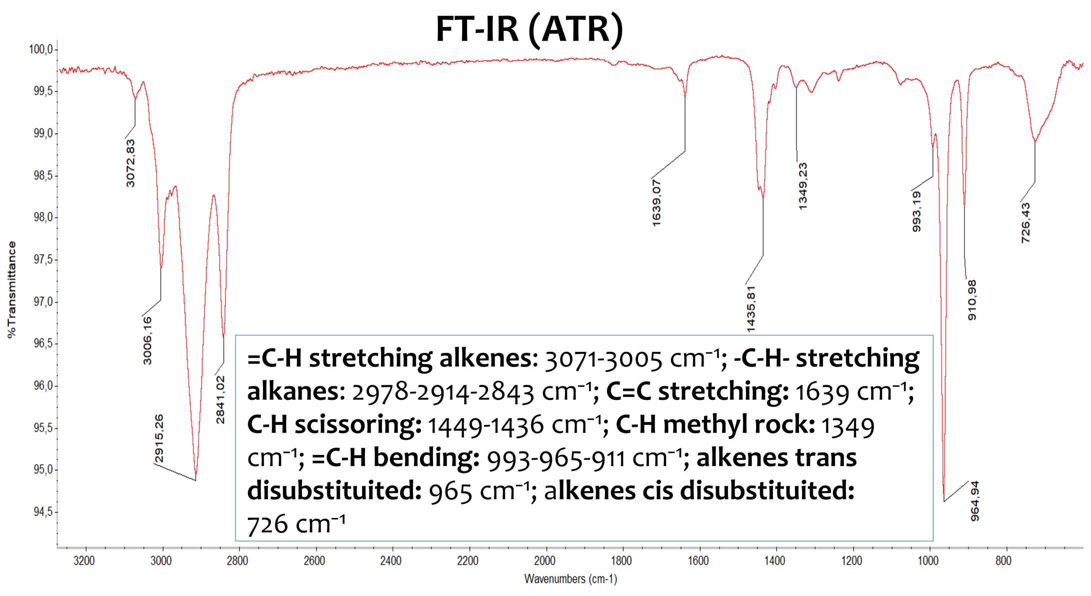
Matrix: LPBD

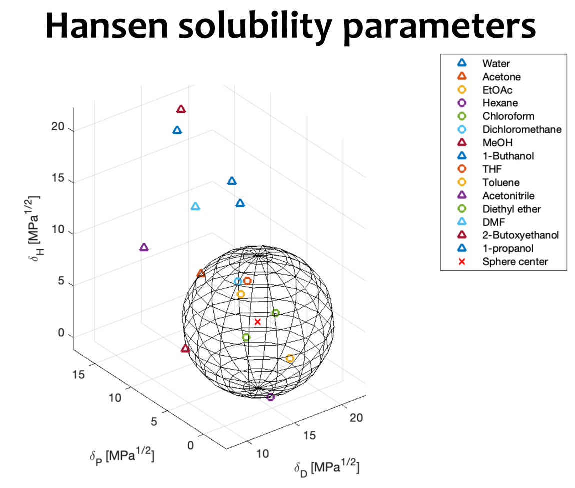
Liquid Polybutadienes (LPBDs) derive from 1,3-butadiene, a highly reactive C4 monomer





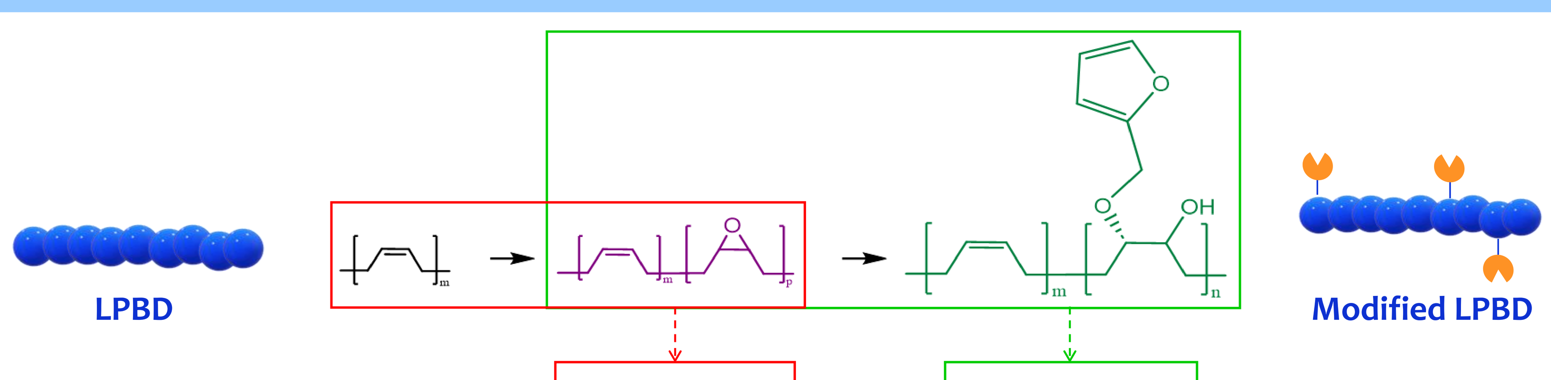
LPBD characterization

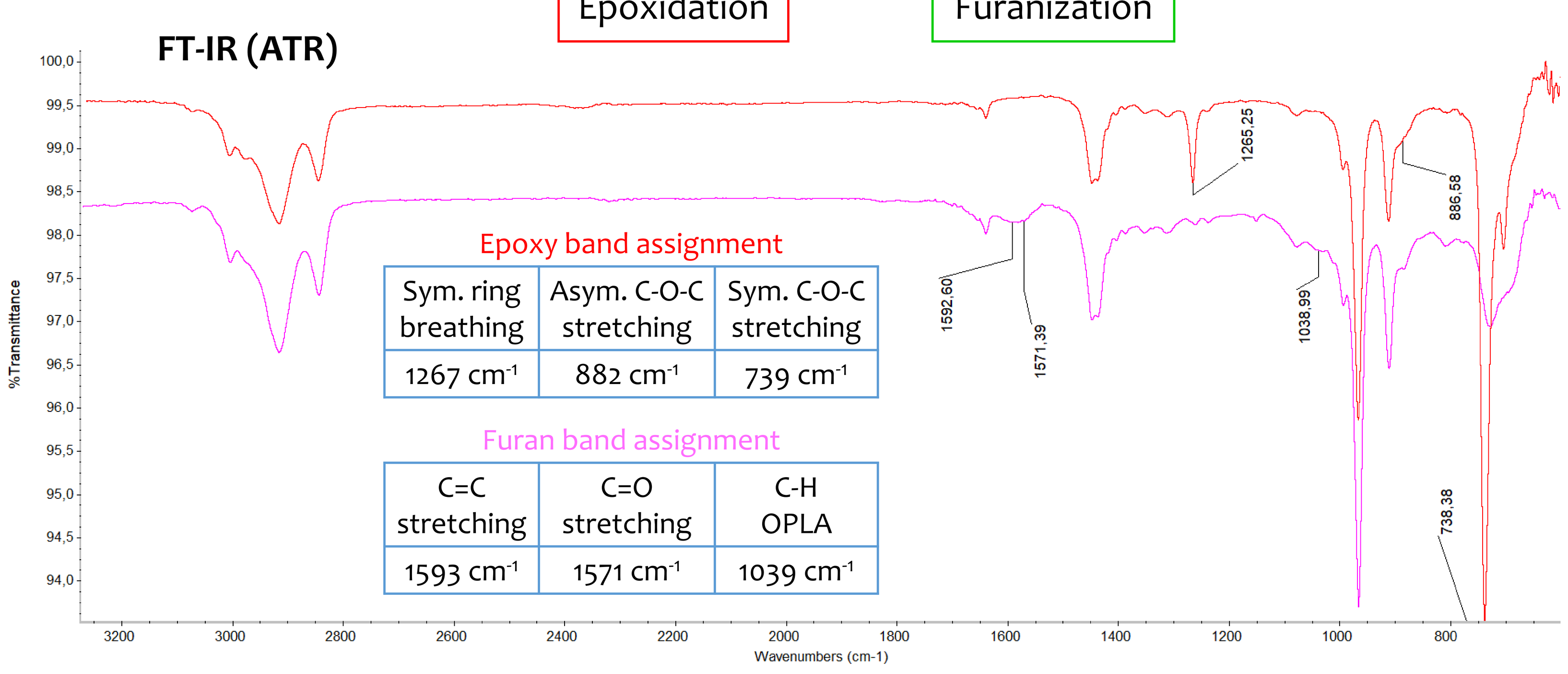




	δ_d	δ_p	δ_h	R_h	δ_t
LPBD	16.1	3.3	5.3	6.4	17.3

Modification of LPBD





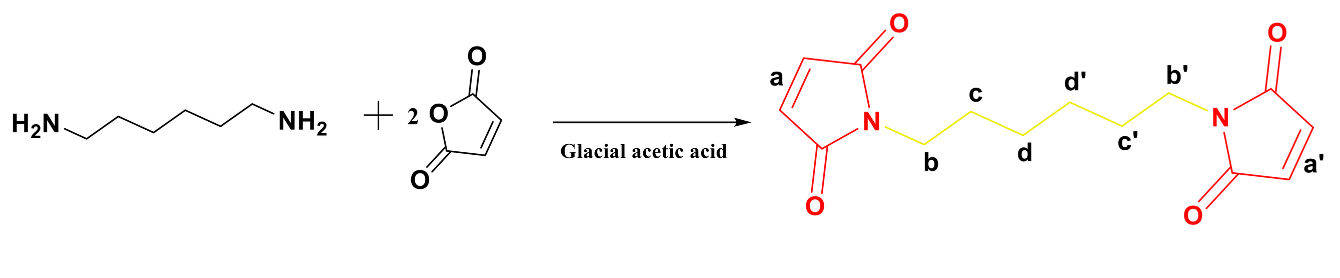
Epoxy band assignment

Sym. ring breathing	Asym. C-O-C stretching	Sym. C-O-C stretching
1267 cm⁻¹	882 cm⁻¹	739 cm⁻¹

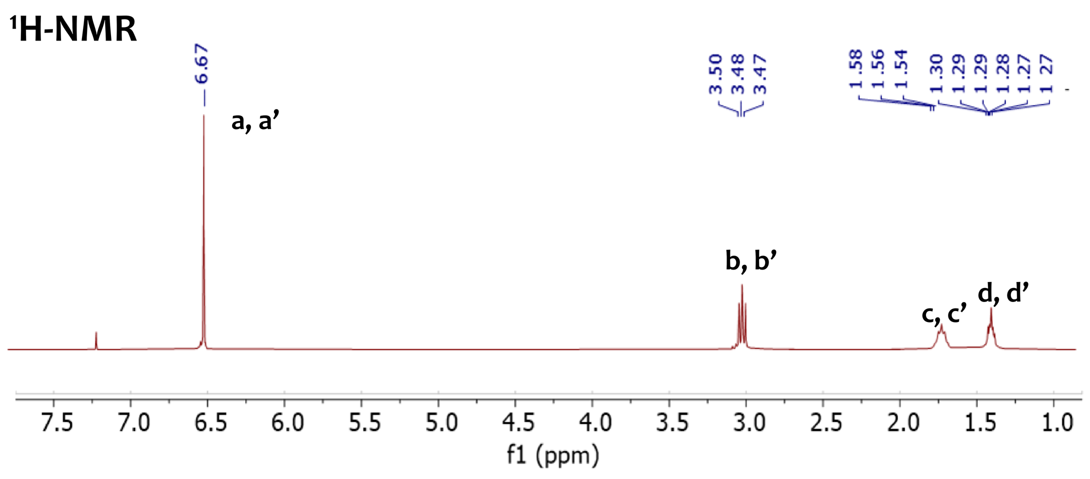
Furan band assignment

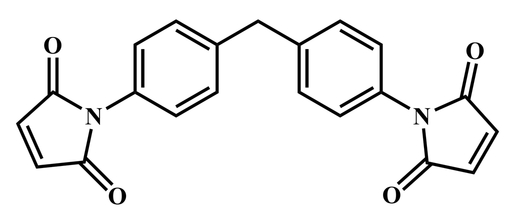
C=C stretching	C=O stretching	C-H OPLA
1593 cm⁻¹	1571 cm⁻¹	1039 cm⁻¹

Synthesis of the crosslinkers



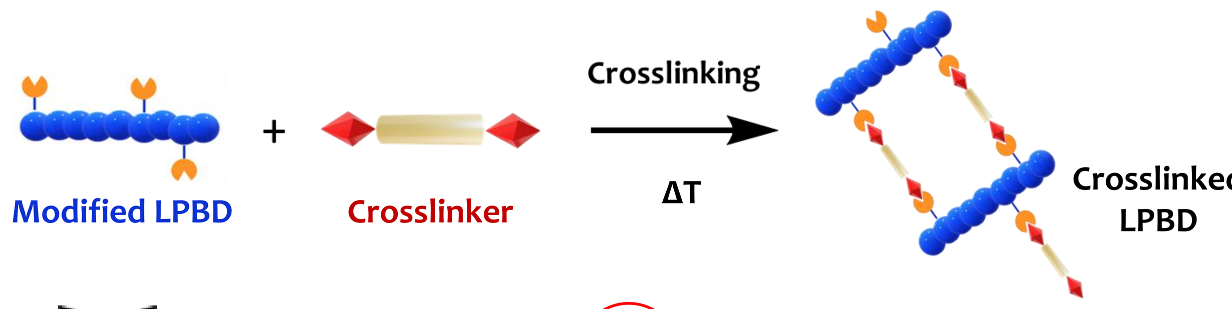
Hexamethylenediamine bismaleimide
BMH



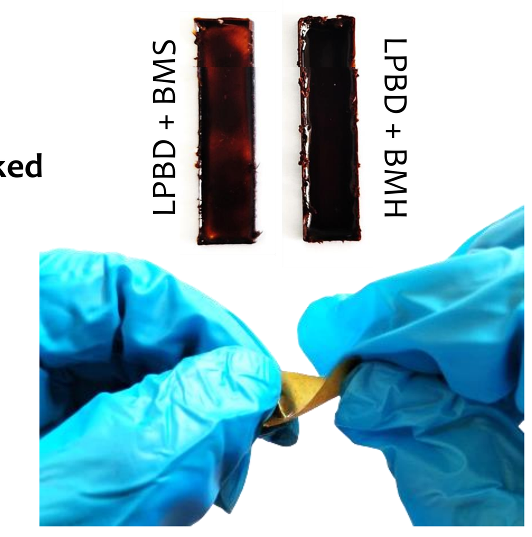


1,1'-(Methylenedi-4,1-phenylene)bismaleimide
BMS

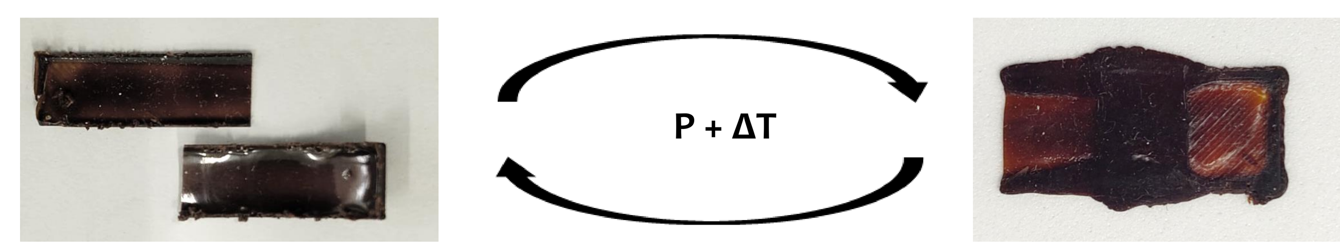
Crosslinking of the LPBD matrix



- Highly stretchable
- Non-adhesive
- Flexible
- Low curing temperature

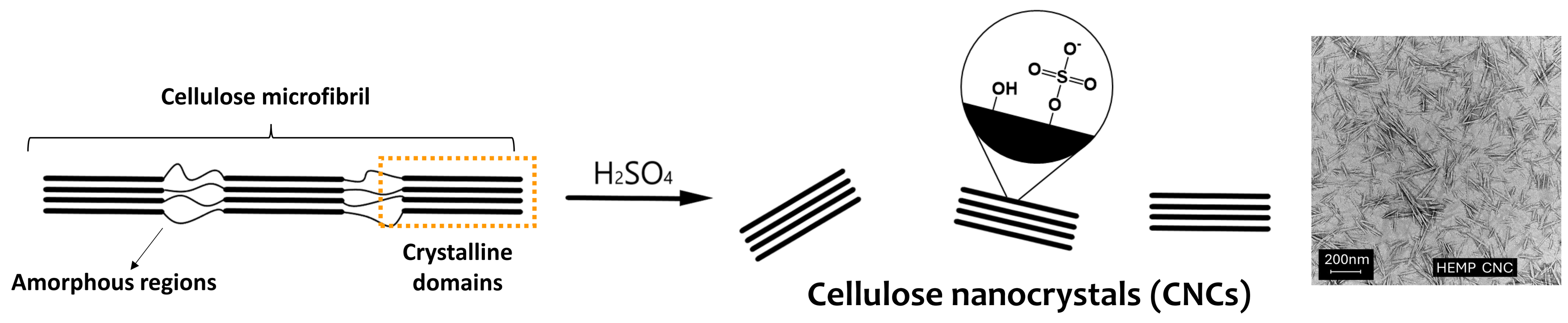


Reshapability test



Successful **reshaping** of the materials through retro Diels–Alder

Biofiller: nanocellulose



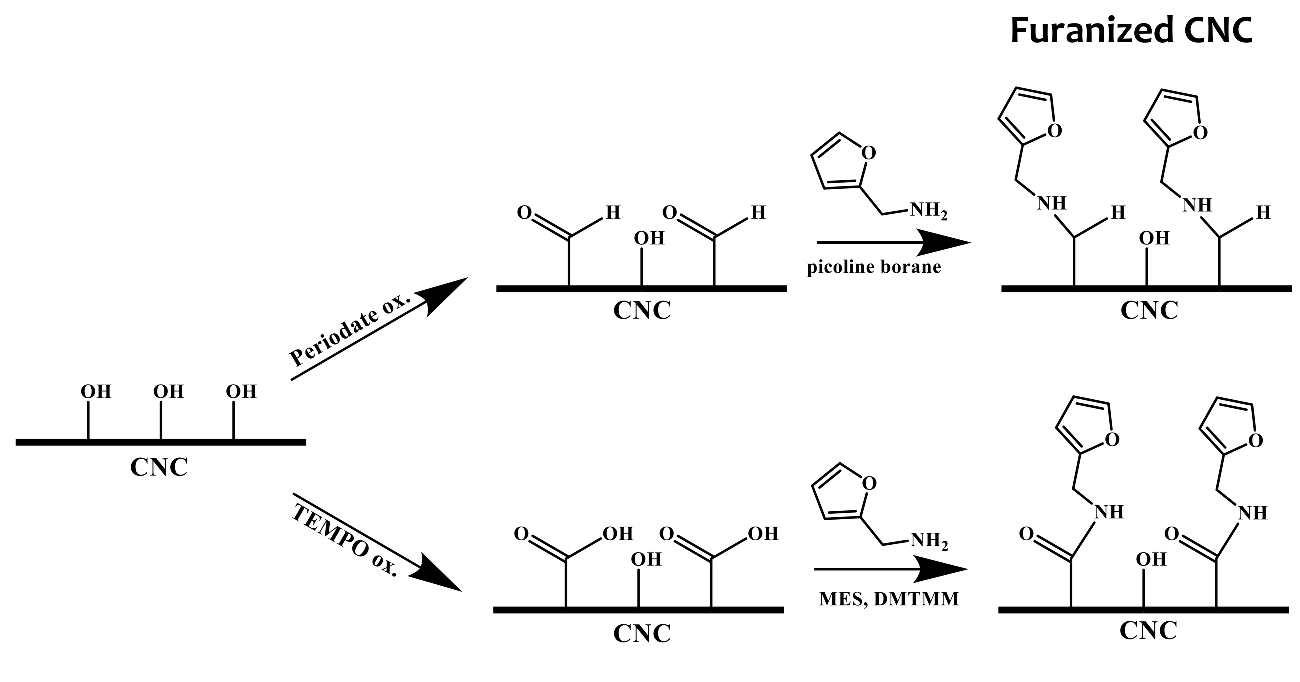
CNCs were extracted from different cellulosic materials:

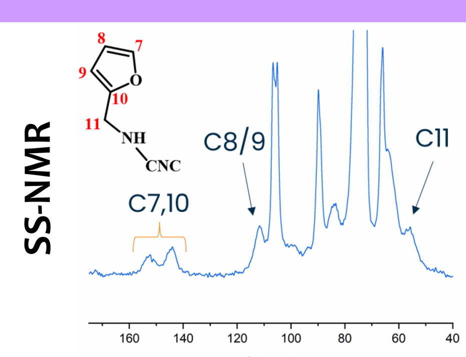
- Hemp pulp – dried cellulose sheets from Delfort®
- Microcrystalline cellulose (MCP) – powder from Technocel®
- Microfibrillated cellulose (MFC) – paste from Exilva®

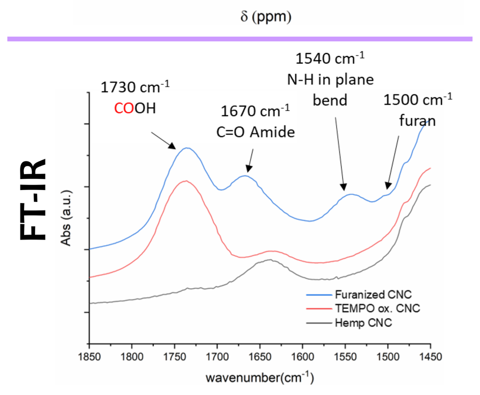
CNCs are characterized by

- High surface area
- High aspect ratio
- Excellent mechanical proprieties

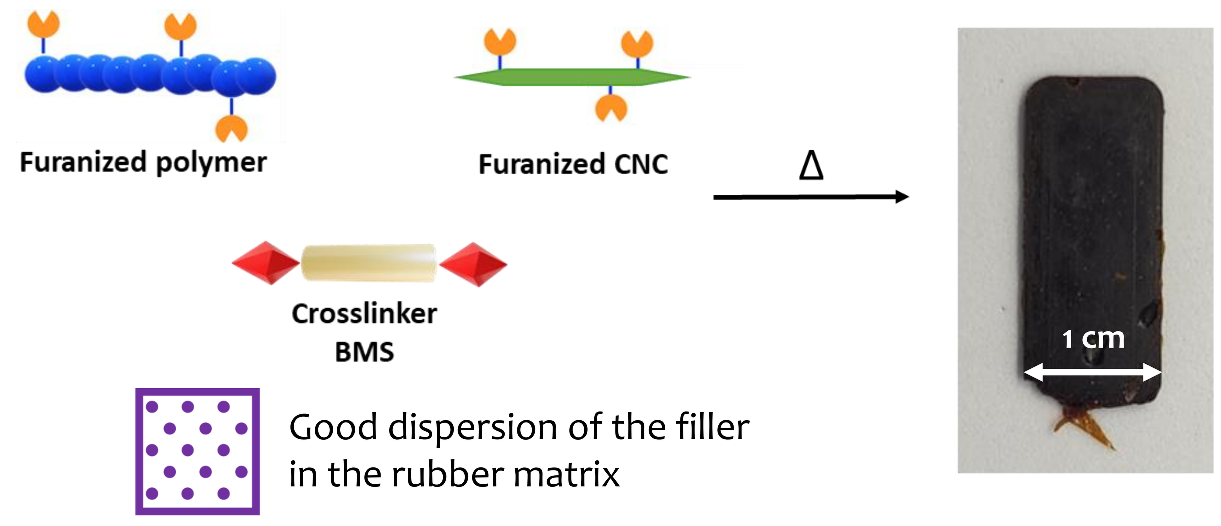
Nanocellulose modification



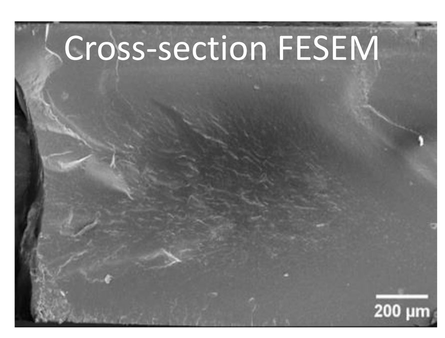




Composite preparation



Good dispersion of the filler in the rubber matrix



Absence of large aggregate of CNCs

Conclusion and future prospectives

The modification of liquid rubber was successfully achieved, and the dienophile for the Diels–Alder reaction was synthesized. The resulting crosslinked rubber material showed both excellent flexibility and high stretchability. Notably, its reshaping and reprocessing capabilities via dynamic covalent Diels–Alder chemistry were clearly demonstrated. Crystalline nanocellulose was effectively extracted and subsequently functionalized through furanization using two distinct synthetic approaches. Additionally, preliminary reversibly crosslinked rubber composites containing the functionalized bio-filler were prepared.

Looking ahead, the reaction conditions for the Diels–Alder and retro-Diels–Alder processes, as well as the furan-to-maleimide molar ratios, will be systematically optimized to enhance the crosslinking density and mechanical performance of the rubber composites. Furthermore, these reversibly cured elastomeric composites will be explored as flexible electronic substrates, offering a promising alternative to the thermoset materials currently in use.

References

[1] N. Zheng et al. Chem. Rev. 121, 1716 (2021)
[2] P. Chakma et al. Angew. Chem. Int. Ed. 58, 9682 (2019)
[3] Z. Wang et al. Acc. Chem. Res. 50, 1762 (2017)

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