Lignosulfonates and 5-hydroxymethylfurfural (HMF) as formaldehyde-free adhesion promoters in fiber-reinforced elastomer products

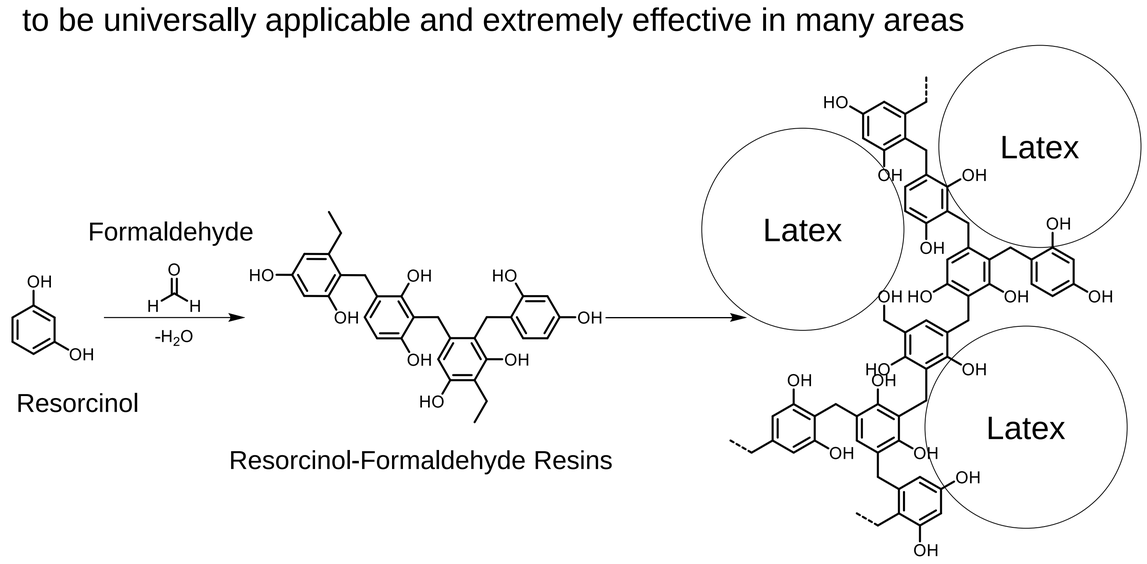
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Problem Description

- An excellent adhesion between high-tenacity fibers (e.g. cord) and the matrix is a must in many areas of fiber-reinforced technical elastomer products in order to prevent delamination of the composite under stress
- Resorcinol-Formaldehyde Latex (RFL) adhesion promoter dips have proven to be universally applicable and extremely effective in many areas



- Formaldehyde: carcinogenic, not eco-friendly, causes allergic reactions
- Resorcinol: potentially hormonally active, smell, possible carcinogenic substances

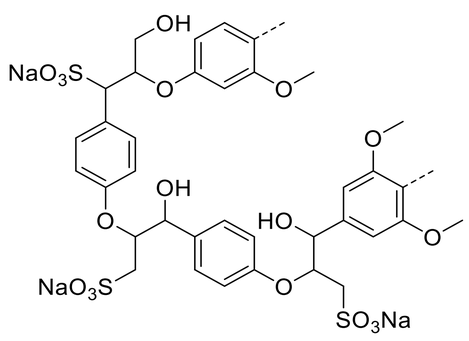
Research Goals

- Substitution of formaldehyde and resorcinol by non-hazardous and sustainable chemicals
- Development of an adhesive chemistry based on bio-based platform chemicals
- Formation of bio-based covalently crosslinked and interpenetrating networks in the sector of high tenacity yarn reinforced elastomeric matrices

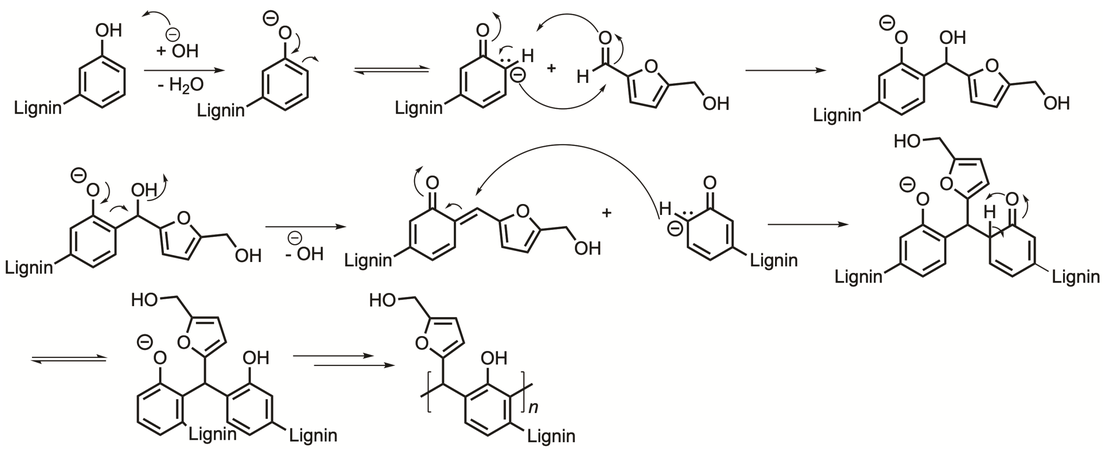
Bio-based Alternatives to Conventional RFL

- **5-HMF** is a naturally occurring platform chemical derived from carbohydrates and shows no carcinogenic effect
- **Lignosulfonates** are derived from lignin, the second most abundant natural biopolymer and represent a renewable resource with significant potential as an alternative to fossil-based materials.





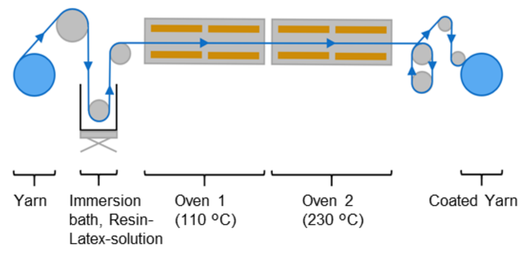
- **Resin formation:** Under alkaline conditions, phenolic groups of lignosulfonates react with HMF via hydroxymethyl intermediates and subsequent condensation reactions, forming a covalently crosslinked resin network.



Proposed reaction mechanism for the formation of lignosulfonate-HMF resins under alkaline conditions.

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Yarn Dipping Process

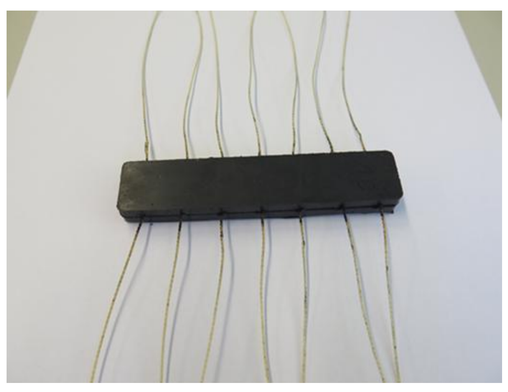


Application of the dips as a pad-dry-cure process.

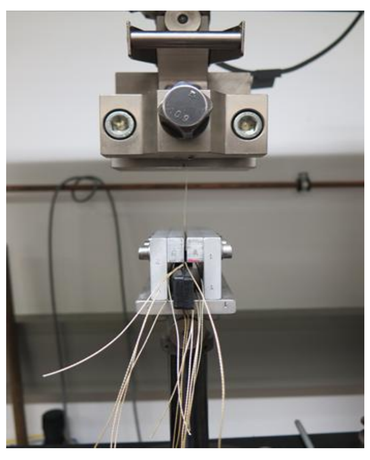


Filament coating line at the DITF Denkendorf with dipping of PES cord.

Composite Construction and Testing



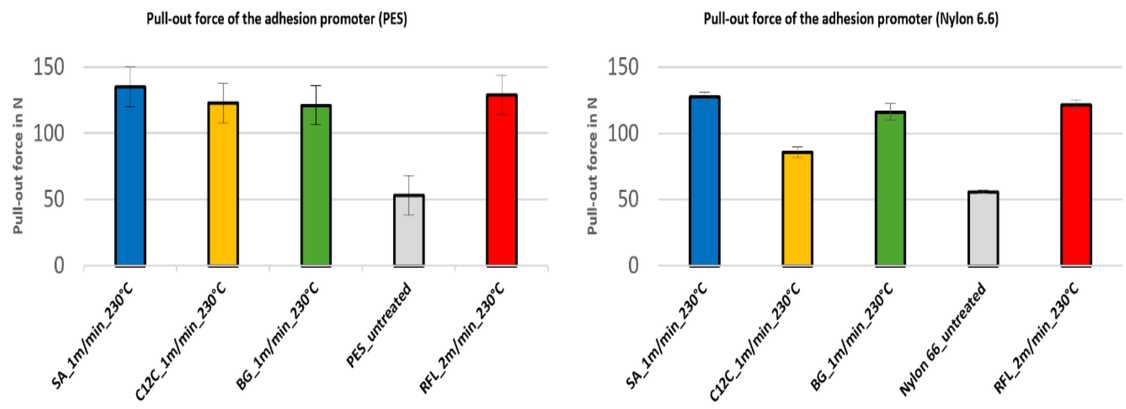
Samples are cured at 170°C, 16 min, 6 bar in heating press.



Static pull-out test (Zwick) performed after storage in standard climate (24h, 20°C, 65% humidity).

Pull-out Test Results for PES and Nylon 6.6 Cord / NR-SBR Composite

100% HMF / three different lignosulfonate dips on PES and nylon 6.6 cord



Pull out force of coated PES yarns (left) and pull-out force of coated nylon 6.6 yarns (right). Lignosulfonate HMF latex system based on lignosulfonic acid SA, lignosulfonate C12C and lignosulfonate BG compared with untreated references and a conventional RFL system.

Conclusions and Outlook

- As a substitute for formaldehyde, HMF has proven itself as a bio-based, non-toxic alternative in adhesives for technical applications
- Bio based substances such as lignosulfonates can be used as alternatives to resorcinol
- However, further research is needed to ensure that these resins ultimately match the technical behavior of resorcinol formaldehyde resins, and also with respect to the plurality of rubbers and other elastomeric matrices
- The development of combined non-toxic predip/dip systems for PES and *p*-aramids, which can be applied in a one-step process, is a challenge in further work

Acknowledgments

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