

Crosslinking and Carbonization of Electrospun Lignosulfonate Fiber



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Motivation

Submicron-sized fiber of lignosulfonate can be electrospun from aqueous solution, signifying the possibility of green processing for biobased polymer. The resulted fiber, however, is susceptible to the influence of water, which limits its use for wet applications such as water filtration.

This poster reports our ongoing efforts in utilizing lignin waste for aqueous filtration and related applications by conversion to electrospun fiber

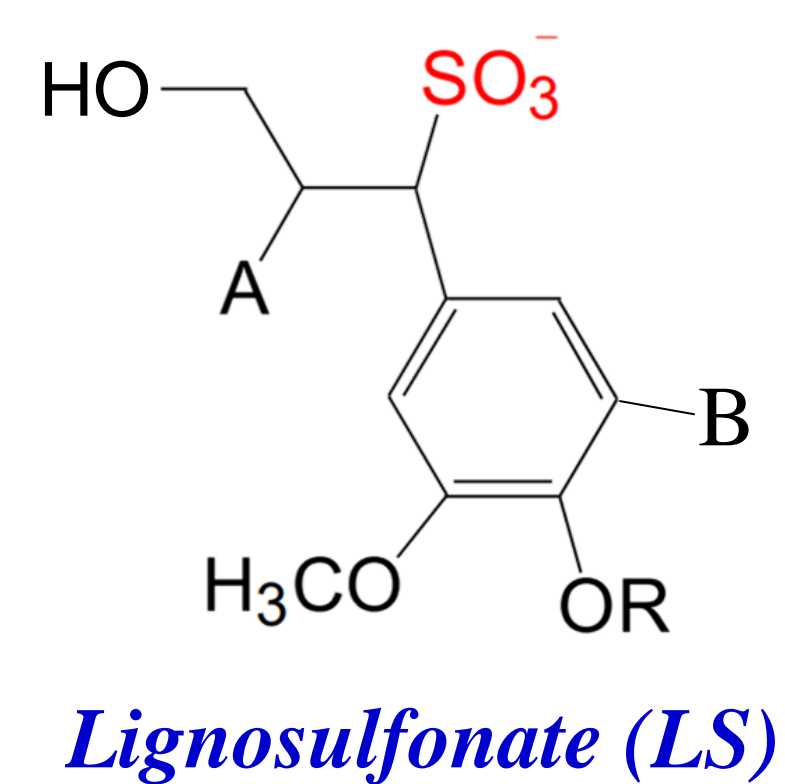
Objectives

- 1) Investigate the effects of crosslinking on the water resistance of electrospun fiber.
- 2) Study thermal stability of the crosslinked fiber, paving the way for facilitating its further conversion to carbon fiber and related products.

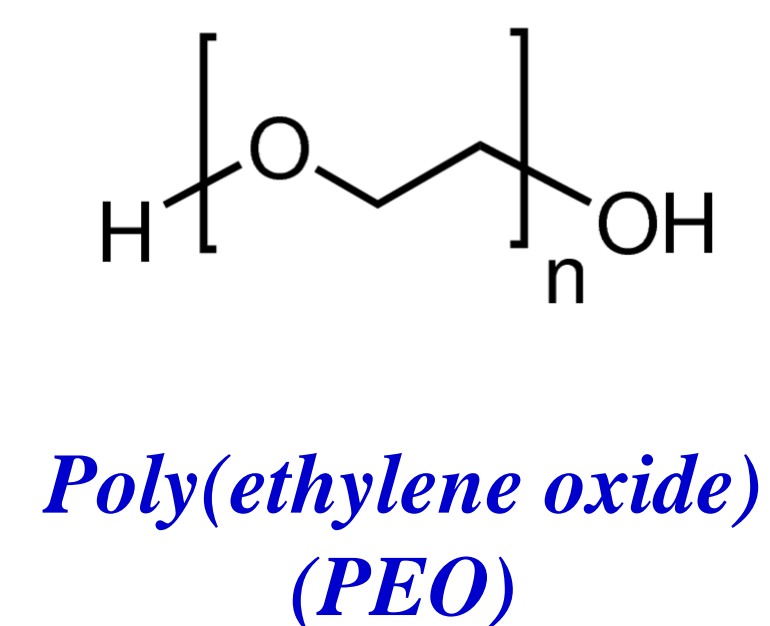
Materials and Methods

• **Spinning material:** 1) Sodium lignosulfonate from hardwood (Borregaard); M_w 8,000 g/mol

• **Additive:** 1) Poly(ethylene oxide) as fiber former; supplied by Acros; M_w 600,000 g/mol
2) Citric acid (Showa) as biobased crosslinker



$R = H \text{ or } LS;$
 $A = 0, H, \text{ or } LS;$
 $B = H, OCH_3, \text{ or } LS$

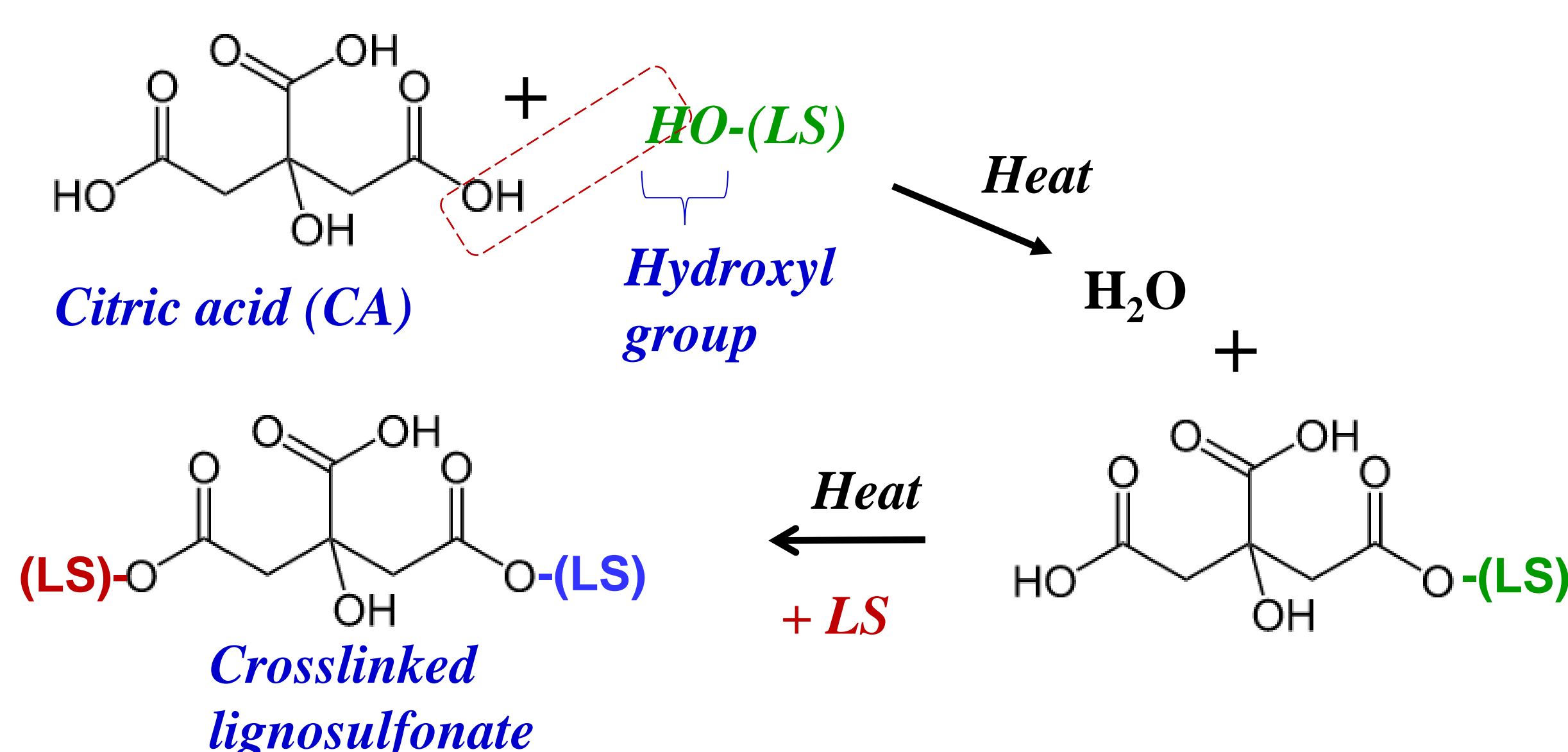


LS structure modified from: Ye et al. (2017) BioResources 12(3):4810-4829.

• **Spinning condition:** Aqueous solution (15-20% solid content) of 0.03 mL/min flow rate horizontally spun at 20 kV (EL50P0 Glassman High voltage) onto a rotating (250 rpm) drum (15 cm width) that is 20 cm away from the injector

• **Crosslinking condition:** Chemical crosslinking (citric acid 140°C for 2h) or, for references, (i) no crosslinker but heated in the same manner, (ii) conventional oxidative crosslinking (in this case, heating at 1°C/min; 300°C for 30 min)

Anticipated reaction with citric acid



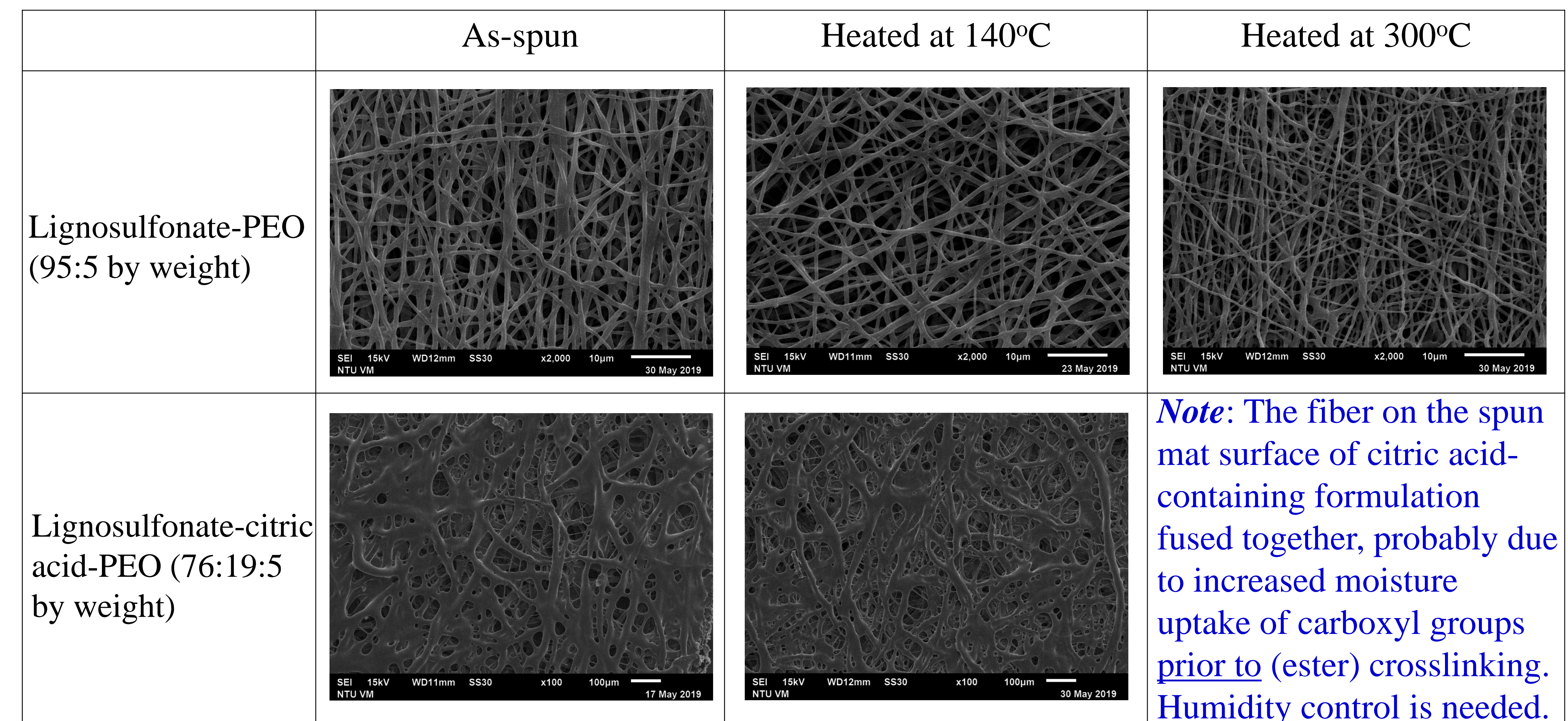
Concept of oxidative crosslinking

This process involves heating in air (or oxygen) at a slow rate to induce demethoxylation reactions, degrade/convert inter-unit linkages or aliphatic side-chain functionality of lignin, and form carbonyl and carboxyl groups^[1]. The oxygenated groups are inserted into linkages in lignin to impart crosslinking, improve thermal stability, and prevent melting.

^[1] Souto et al. (2018) Mater. Res. Express 5:072001

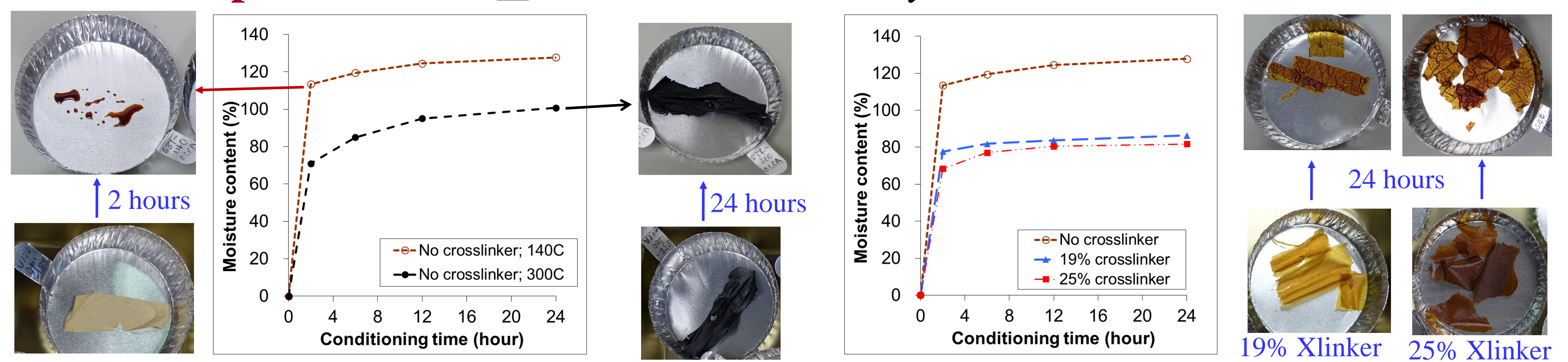
Results & Discussion

Morphology study: Scanning electron microscopy (Jeol JSM 6510) at 15 kV



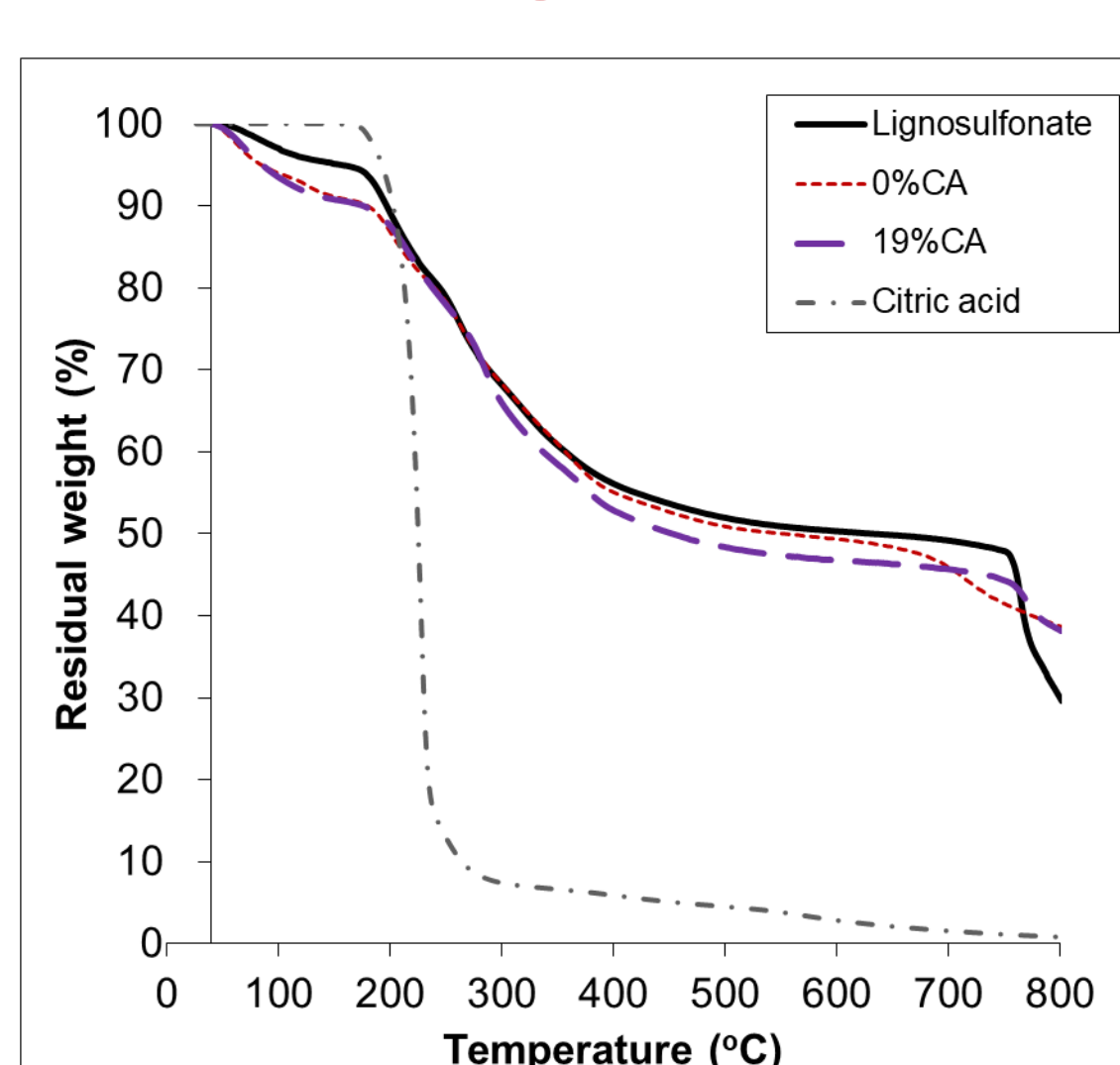
Note: The fiber on the spun mat surface of citric acid-containing formulation fused together, probably due to increased moisture uptake of carboxyl groups prior to (ester) crosslinking. Humidity control is needed.

Moisture uptake test: 95±1% at 23°C in Terchy environmental test chamber



Observation: Moisture resistance can be induced by either chemical crosslinking (140°C) or thermal oxidative crosslinking (300°C). Crosslinking prevents dissolution. Citric acid at the tested dosages reduced moisture uptake by up to 40% (versus 20% in oxidative) after 24-h exposure.

Thermogravimetric analysis (TGA): Inference on carbonization



Instrument: Mettler-Toledo TGA/SDTA85e; 10°C/min in nitrogen

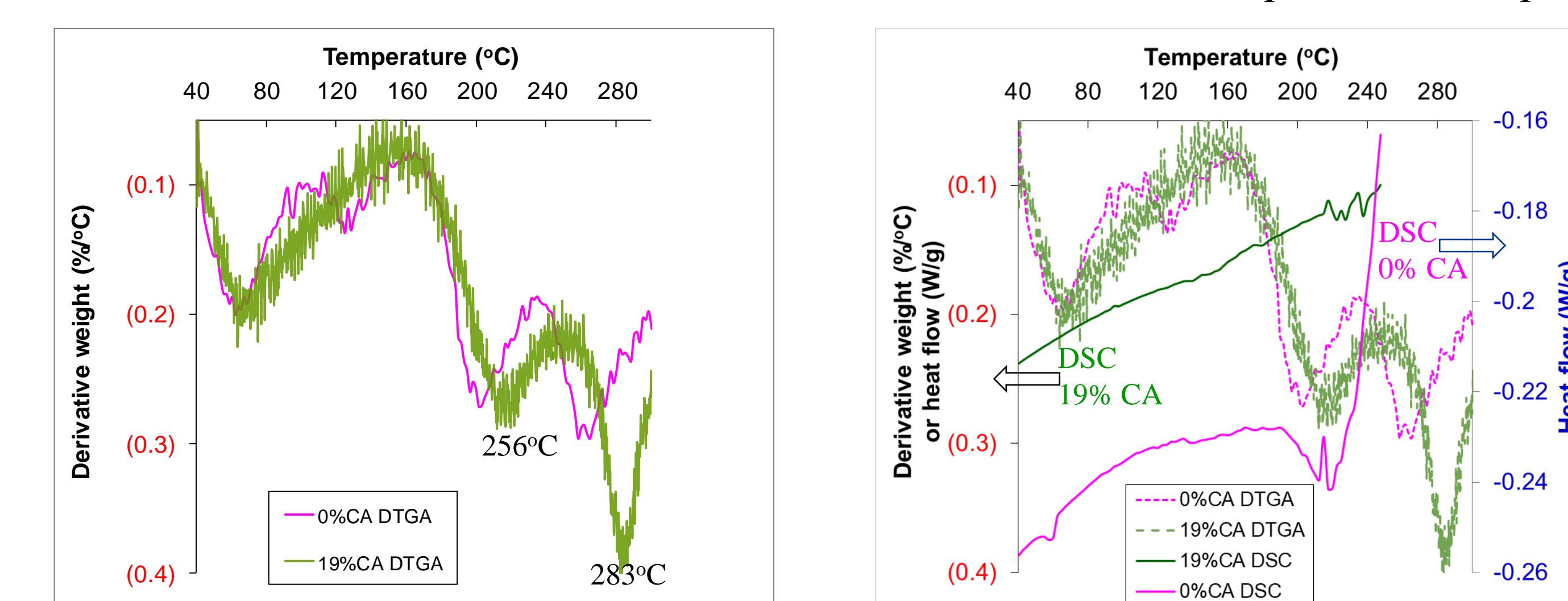
	$T_{max \text{ rate}^*}$ (°C)	Wt. loss (%) 170-375°C	Wt. loss (%) 375-700°C	Char (%) at 700°C
Lignosulfonate	257	37	9	49
LS-PEO (95:5)	256	34	11	46
LS-PEO-citric acid (76:5:19)	283	35	9	46
Citric acid	229	94	5	1.6

*From DTGA; see example plots in DSC section

Note: The char yields of spun fibers do not differ much. Crosslinking with citric acid resulted in maximum degradation rate* occurring at a higher temp (also higher than that of citric acid alone).

Differential scanning calorimetry (DSC)

Instrument: Mettler-Toledo DSC823e; 10°C/min; the second temperature ramp curves were analyzed



Note: DTGA data are presented here to possibly relate DCS profile to thermal degradation

Attempts to examine manifestation of crosslinking was hampered by vague transitions and broad peaks in DSC curves of lignosulfonate. Peaks at ~100°C was due to residual water removal^[2]. Above 170°C (up to 250°C measured), larger exothermic peaks corresponding to DTGA peaks are seen, suggesting liberation of degraded products from thermal degradation.

^[2] Da Silva et al. (2012) TAPPI 11(9):41-49.

Conclusions

We succeeded in using a biobased crosslinker to resist dissolution and improve water resistance of lignosulfonate. The electrospinning protocol for preparing the crosslinked fiber has yet to be refined. Efforts are underway to spin the fiber on porous supporting materials for aqueous filtration tests.

Acknowledgement

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