**Supporting Information for publication**

# Lignin-modified tunicate cellulose nanofiber (CNF)-starch composites: impact of lignin diversity on film performance

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**Table S1.** Composition and specific structural features of lignin fractions (by Py-GC/MS-FID)

| | | | Initial | EtOAc | EtOH | MeOH | Acetone | Insoluble |
|---|---|---|---|---|---|---|---|---|
| Spruce | Carbohydrates (C) | %, from chromatogram | 2.5 | 2.5 | 2.0 | 2.1 | 1.7 | 7.0 |
| | Lignin derivates (L) | | 46.4 | 48.9 | 45.1 | 40.2 | 42.6 | 38.3 |
| | Summary: C+L = 100% | | 48.9 | 51.4 | 47.1 | 42.3 | 44.3 | 45.2 |
| | Summary: Carbon dioxide, Methanal, Water, Methanol | | 46.7 | 43.9 | 47.4 | 52.4 | 51.9 | 51.2 |
| | S-containing | | 2.7 | 1.8 | 2.3 | 3.3 | 2.3 | 2.3 |
| | Carbohydrates (C) | %, from C+L | 5.1 | 4.8 | 4.3 | 4.9 | 3.9 | 15.4 |
| | Acid, Ester | %, from C | 26.2 | 23.5 | 31.9 | 31.6 | 39.7 | 20.5 |
| | Aldehyde, Ketone | | 21.0 | 13.0 | 16.7 | 10.1 | 21.3 | 39.2 |
| | Cyclopentane derivates | | 28.6 | 45.8 | 27.9 | 21.5 | 20.1 | 9.6 |
| | Furan | | 21.8 | 17.8 | 22.6 | 34.0 | 18.4 | 21.4 |
| | Pyran | | 2.4 | 0 | 1.0 | 2.9 | 0.6 | 4.2 |
| | Sugars | | 0 | 0 | 0 | 0 | 0 | 5.2 |
| | Lignin derivates (L) | %, from C+L | 94.9 | 95.2 | 95.7 | 95.1 | 96.1 | 84.6 |
| | P and B derivates | %, from L | 16.2 | 15.4 | 15.4 | 17.8 | 17.3 | 14.7 |
| | G derivates | | 83.8 | 84.6 | 84.6 | 82.2 | 82.7 | 85.3 |
| Eucalyptus | Carbohydrates (C) | %, from chromatogram | 2.0 | 1.5 | 1.8 | 1.7 | 1.3 | 5.9 |
| | Lignin derivates (L) | | 54.8 | 61.2 | 53.4 | 48.2 | 55.1 | 44.1 |
| | Summary: C+L = 100% | | 56.8 | 62.6 | 55.1 | 50.0 | 56.4 | 50.0 |
| | Summary: Carbon dioxide, Methanal, Water, Methanol | | 39.3 | 32.4 | 39.6 | 46.2 | 40.5 | 46.2 |
| | S-containing | | 3.0 | 2.5 | 4.2 | 2.8 | 2.3 | 2.7 |
| | Carbohydrates (C) | %, from C+L | 3.4 | 2.4 | 3.2 | 3.5 | 2.3 | 11.7 |
| | Acid, Ester | %, from C | 35.9 | 57.1 | 47.7 | 44.5 | 54.3 | 22.0 |
| | Aldehyde, Ketone | | 14.9 | 12.1 | 16.5 | 16.8 | 18.6 | 31.7 |
| | Cyclopentane derivates | | 14.9 | 17.5 | 15.9 | 15.0 | 14.7 | 7.4 |
| | Furan | | 16.4 | 9.4 | 11.9 | 21.4 | 12.4 | 22.4 |
| | Pyran | | 2.6 | 0 | 0.6 | 2.3 | 0 | 10.8 |
| | Sugars | | 15.4 | 4.0 | 7.4 | 0 | 0 | 5.8 |
| | Lignin derivates (L) | %, from C+L | 96.6 | 97.6 | 96.8 | 96.5 | 97.7 | 88.3 |
| | P and B derivates | %, from L | 3.5 | 3.6 | 3.9 | 3.5 | 4.3 | 3.1 |
| | G derivates | | 27.3 | 24.9 | 28.7 | 28.7 | 31.7 | 35.7 |
| | S derivates | | 66.3 | 69.1 | 63.9 | 64.1 | 60.6 | 57.1 |
| | G+S derivates | | 93.6 | 94.0 | 92.6 | 92.7 | 92.3 | 92.9 |

**Table S2.** Film thickness (μm) of all lignin-CNF-starch composite films and blank films

| | Initial | EtOAc | EtOH | MeOH | Acetone | Insoluble |
|---|---|---|---|---|---|---|
| Softwood | 13.5 ± 0.7 | 14.4 ± 0.7 | 12.8 ± 0.8 | 14.1 ± 0.8 | 16.3 ± 0.8 | 13.6 ± 0.5 |
| Hardwood | 13.6 ± 1.1 | 14.4 ± 0.7 | 13.8 ± 0.4 | 13.5 ± 0.9 | 14.3 ± 0.8 | 13.9 ± 0.8 |
| Blank | | | 11.8 ± 1.4 | | | |

**Table S3.** Contact angle (°) of all lignin-CNF-starch composite films and blank films

| | Initial | EtOAc | EtOH | MeOH | Acetone | Insoluble |
|---|---|---|---|---|---|---|
| Softwood | 66.2 | 45.8 | 56.7 | 66.1 | 71.9 | 60.1 |
| Hardwood | 60.0 | 50.5 | 59.4 | 61.9 | 68.9 | 53.1 |
| Blank | | | 57.0 | | | |

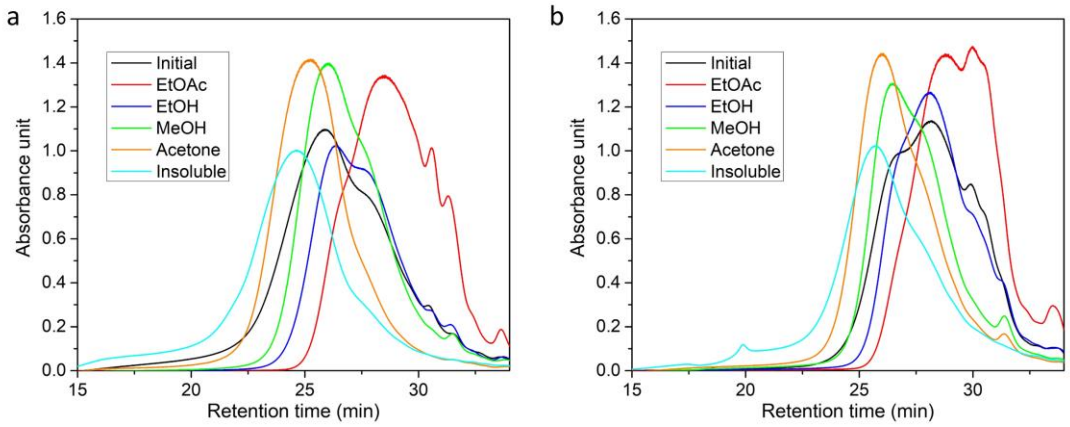


Figure S1. Molecular weight distribution of lignin fractions from softwood (a) and hardwood (b)

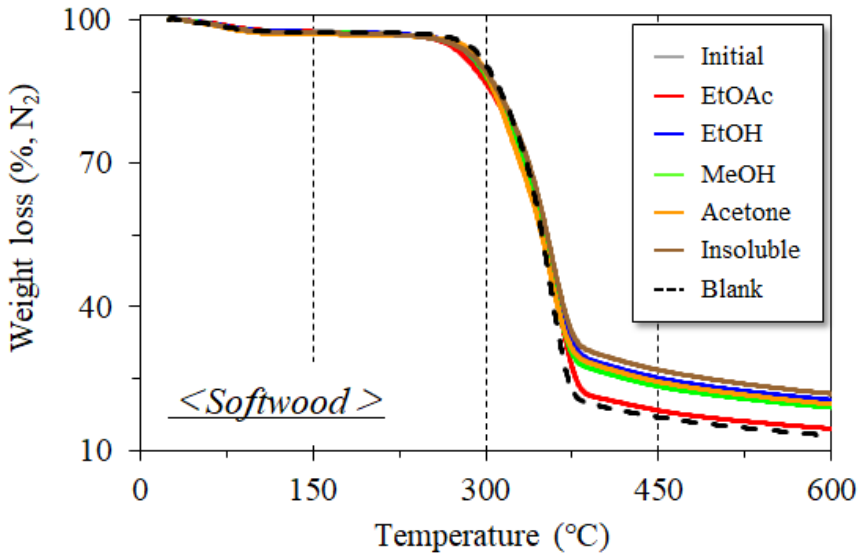


**Figure S2.** The TGA curves of composite films containing softwood lignin fractions ($N_2$ atmosphere)

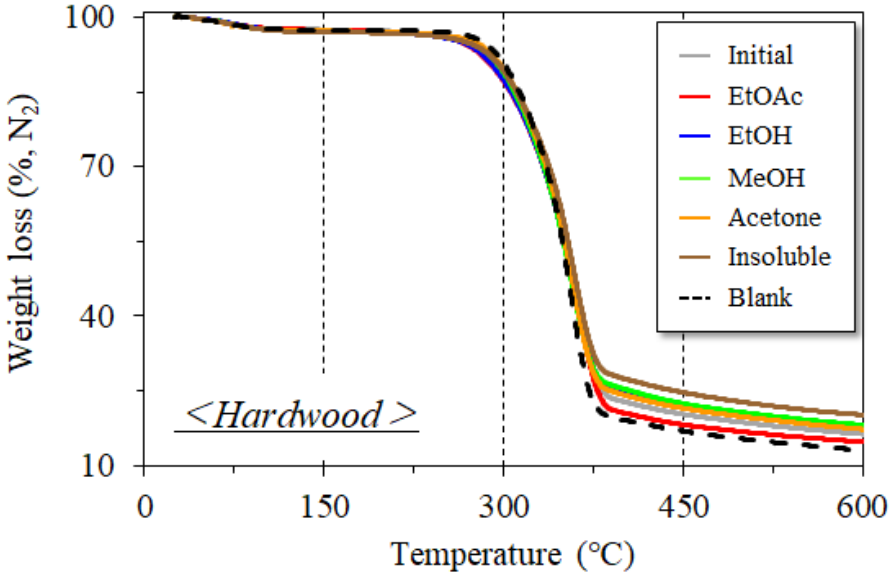


**Figure S3.** The TGA curves of composite films containing hardwood lignin fractions ($N_2$ atmosphere)

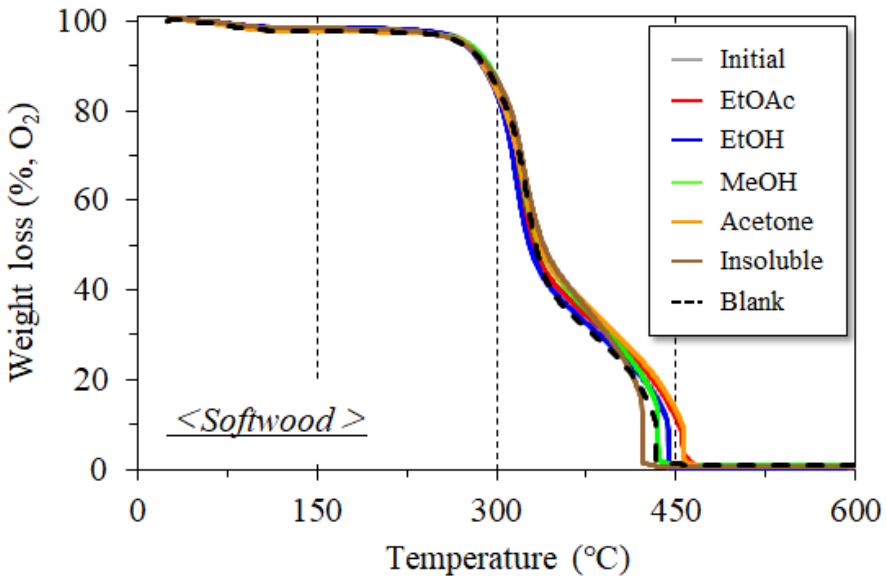


**Figure S4.** The TGA curves of composite films containing softwood lignin fractions ($O_2$ atmosphere)

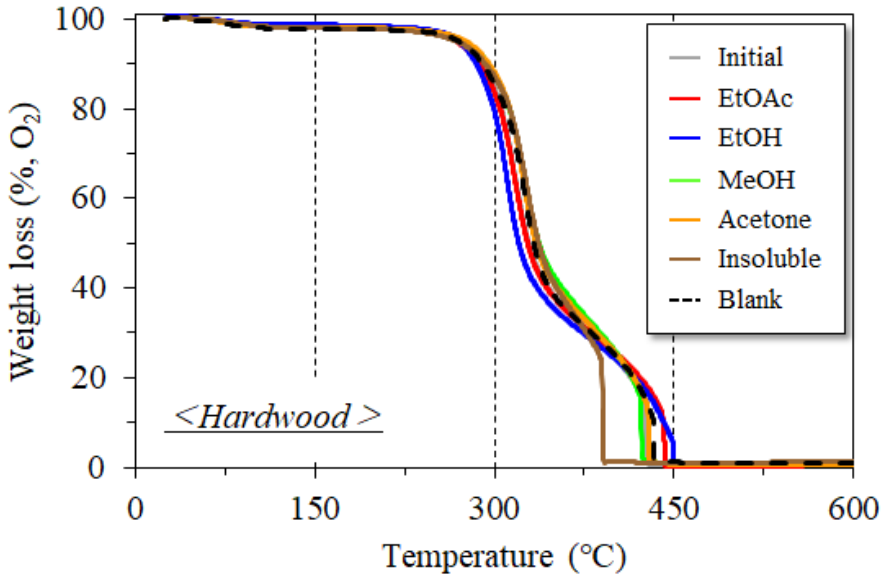


**Figure S5.** The TGA curves of composite films containing hardwood lignin fractions ($O_2$ atmosphere)

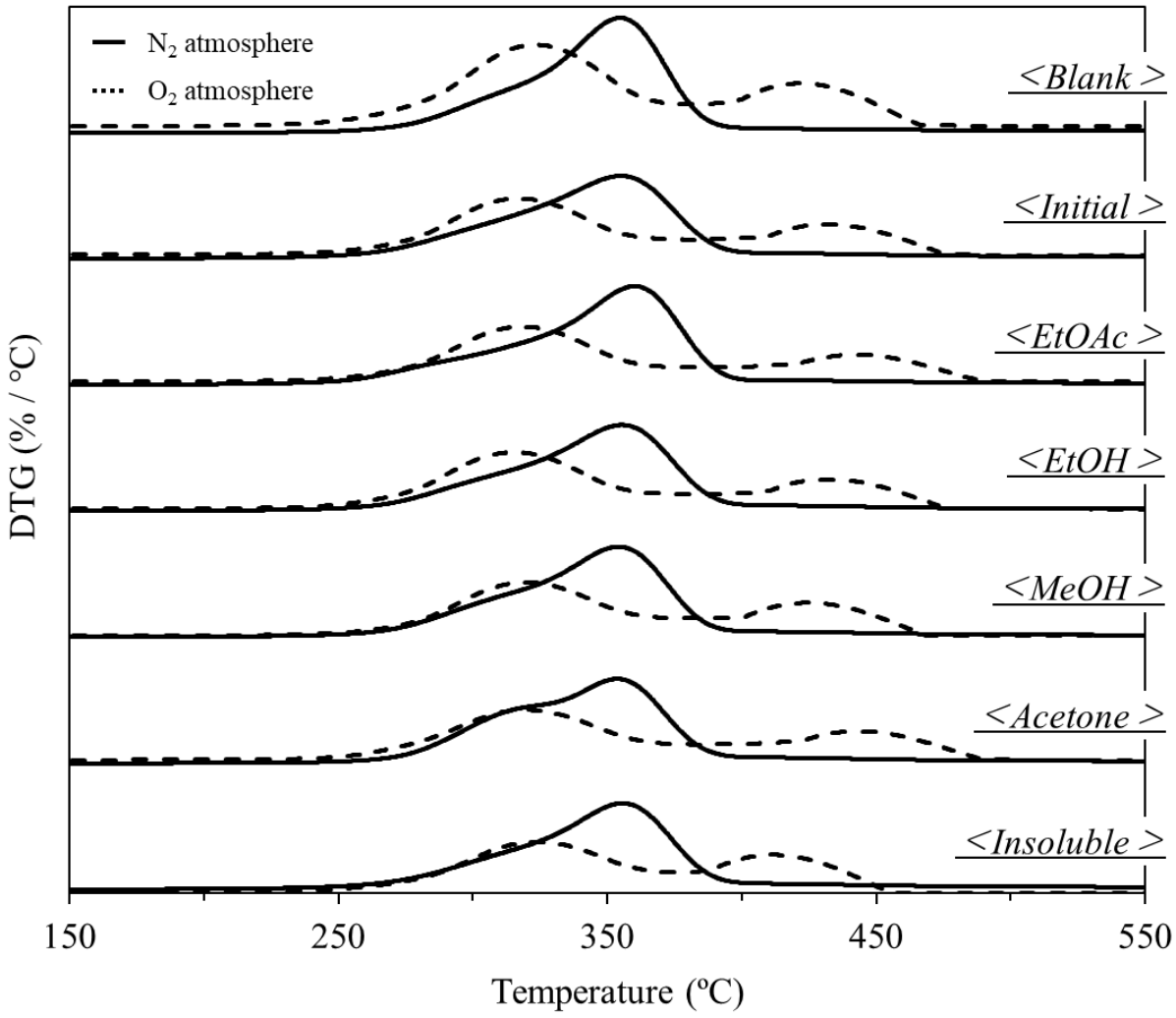


**Figure S6.** The DTG curves of composite films containing spruce lignin fractions (both $N_2$ and $O_2$ atmosphere)

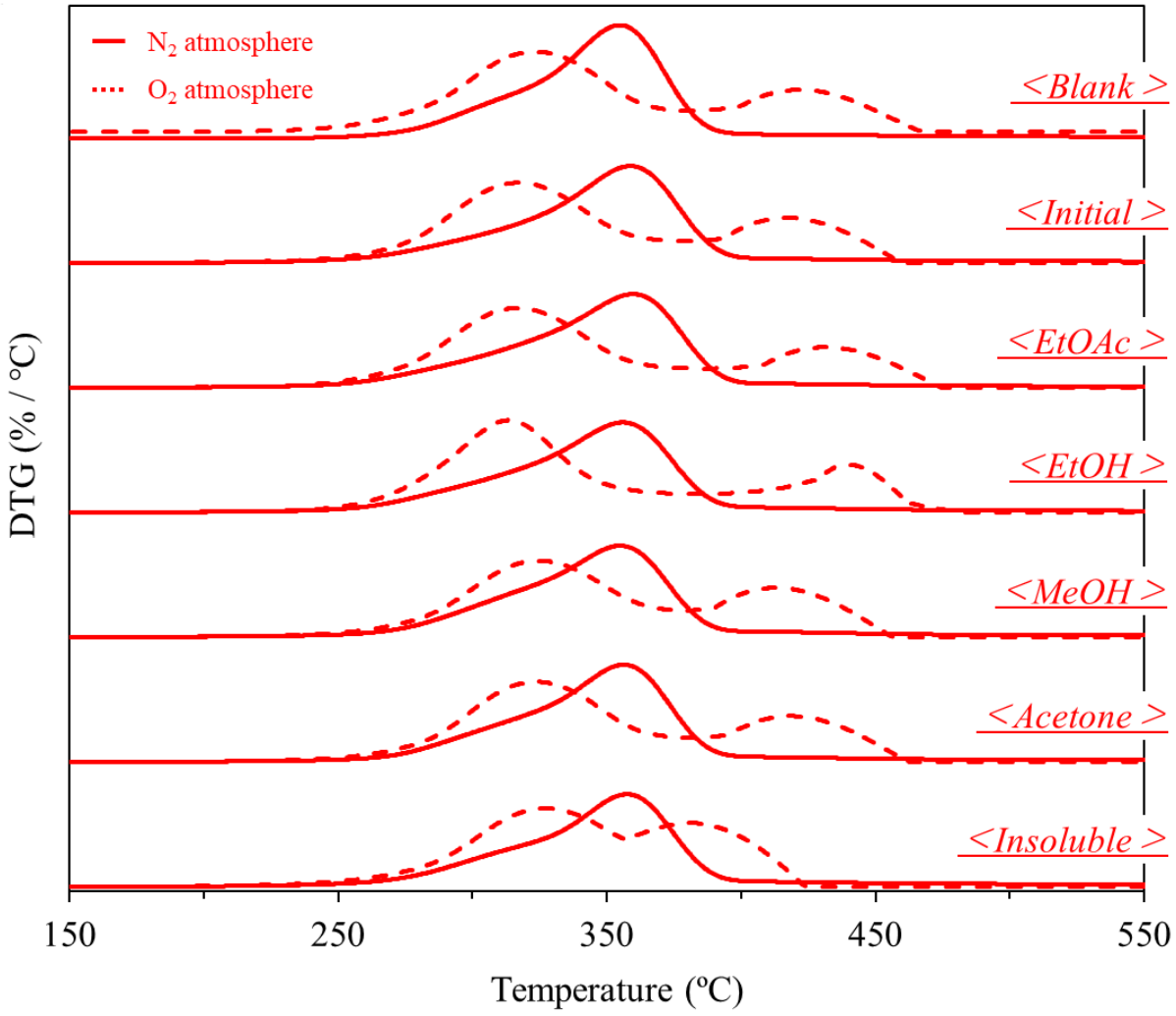


**Figure S7.** The DTG curves of composite films containing eucalyptus lignin fractions (both $N_2$ and $O_2$ atmosphere)

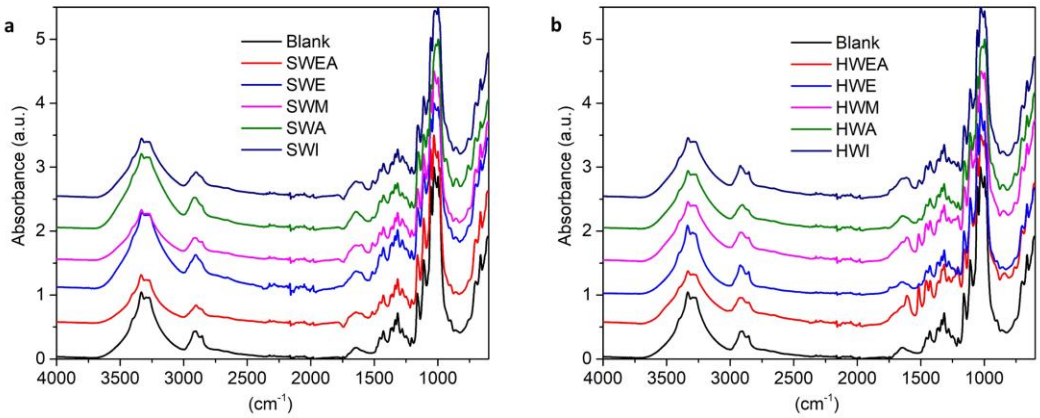


Figure S8. The FTIR spectra of all lignin-CNF-starch composite films and blank films