Addition of Silk Fibroin to Tannin-Furanic Bio-Based Adhesive for Plywood Production

[1]Emanuele Cesprini, [2]Johannes Jorda, [3] Primož Šket, [4]Luca Valentini, [1]Michela Zanetti, [1]Gianluca Tondi

[1] Land Environment Agriculture & Forestry Department, Padova, Italy ; [2] University of Applied Science, Kuchl, Austria , [3] National Institute of Chemistry, Ljubljana, Slovenia; [4] Civil & Environmental Engineering Department, Terni, Italy; *Corresponding Author: emanuele.cesprini@phd.unipd.it

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Introduction

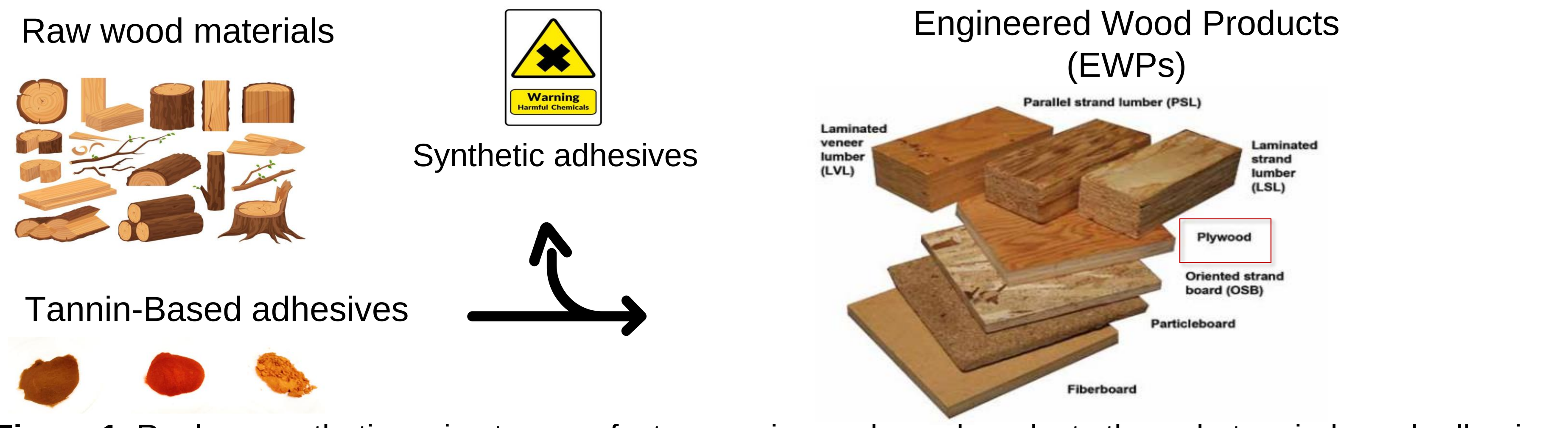

Figure 1. Replace synthetic resins to manufacture engineered wood products through tannin-based adhesive

In order to act against human environmental impact, the transition from non-renewable to sustainable resources is a core pillar:

- Wood and its derivate products may be important resources in multiple areas such as the construction and furniture sectors[1]
- To increase the attractiveness of wood products, natural alternatives to synthetic adhesives are required[2]
- Tannins have been known as possible natural substitutes[3] but important limitations such as stiffness and low moisture resistance still limit their industrial applications
- The intrinsic adhesive properties and toughness of silk fibroin (SF) is proposed to overcame the described issues[4]

Materials and methods

Synthesis of bio-adhesive

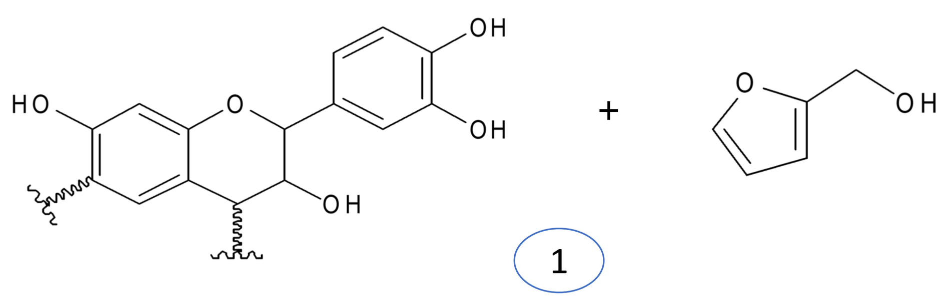

Figure 2. Mixing quebracho powder (Fintan 737) and furfuryl alcohol at 60/40 w/w.

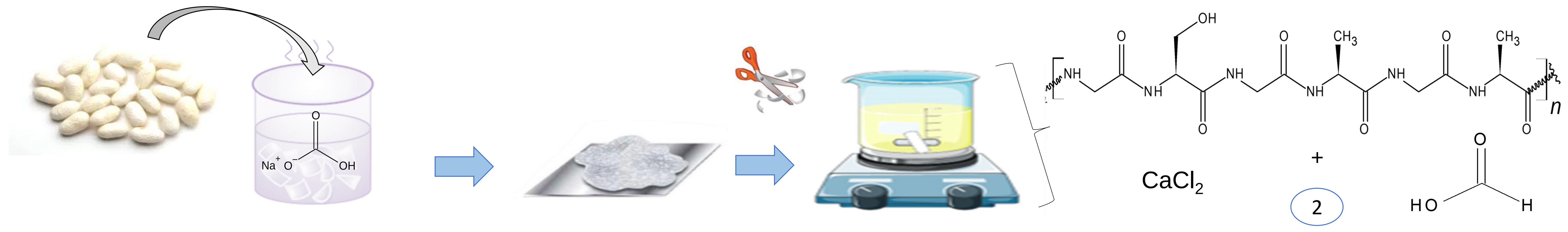

Figure 3. Dissolution of B. Mori cocoons in water solution at 1.6 wt% of sodium bicarbonate at 100°C for 30 minutes. Afterwards, the water insoluble protein (SF) is dissolved in formic acid solution (9 w/w) and with fibroin/calcium chloride 60/40 w/w.

1 + 2

Mixing of tannin-furfuryl alcohol and fibroin solutions at different percentage of protein calculated on tannin amount

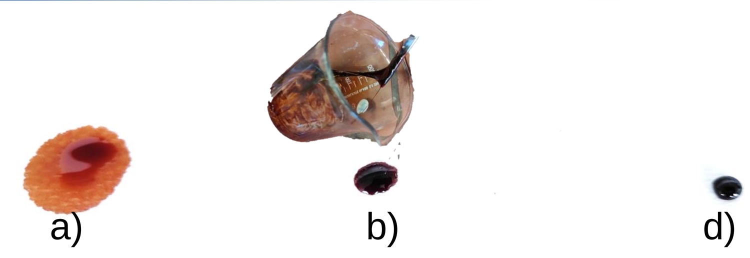

Figure 4. Mixed 1 and 2 solutions to obtain a final formulation at different percentage of fibroin content.

Samples mixing at different fibroin proportions:
a) Reference (without fibroin)
b) 10% of fibroin
c) 15% of fibroin
d) 20% of fibroin
e) 30% of fibroin

Bio-adhesive Characterization and Application

Kinetic behavior of the reactions was investigated through the thermomechanical(TMA) analysis. ^{13}C-NMR was used to understand the chemical interactions between the formulation components. Different samples (a-e) were used to produce of three-layer plywood. Mechanical properties were investigated through wet and dry shear strength(SS), modulus of rupture(MOR), modulus of elasticity(MOE).

Results and discussion

Kinetics behavior of adhesive formulations

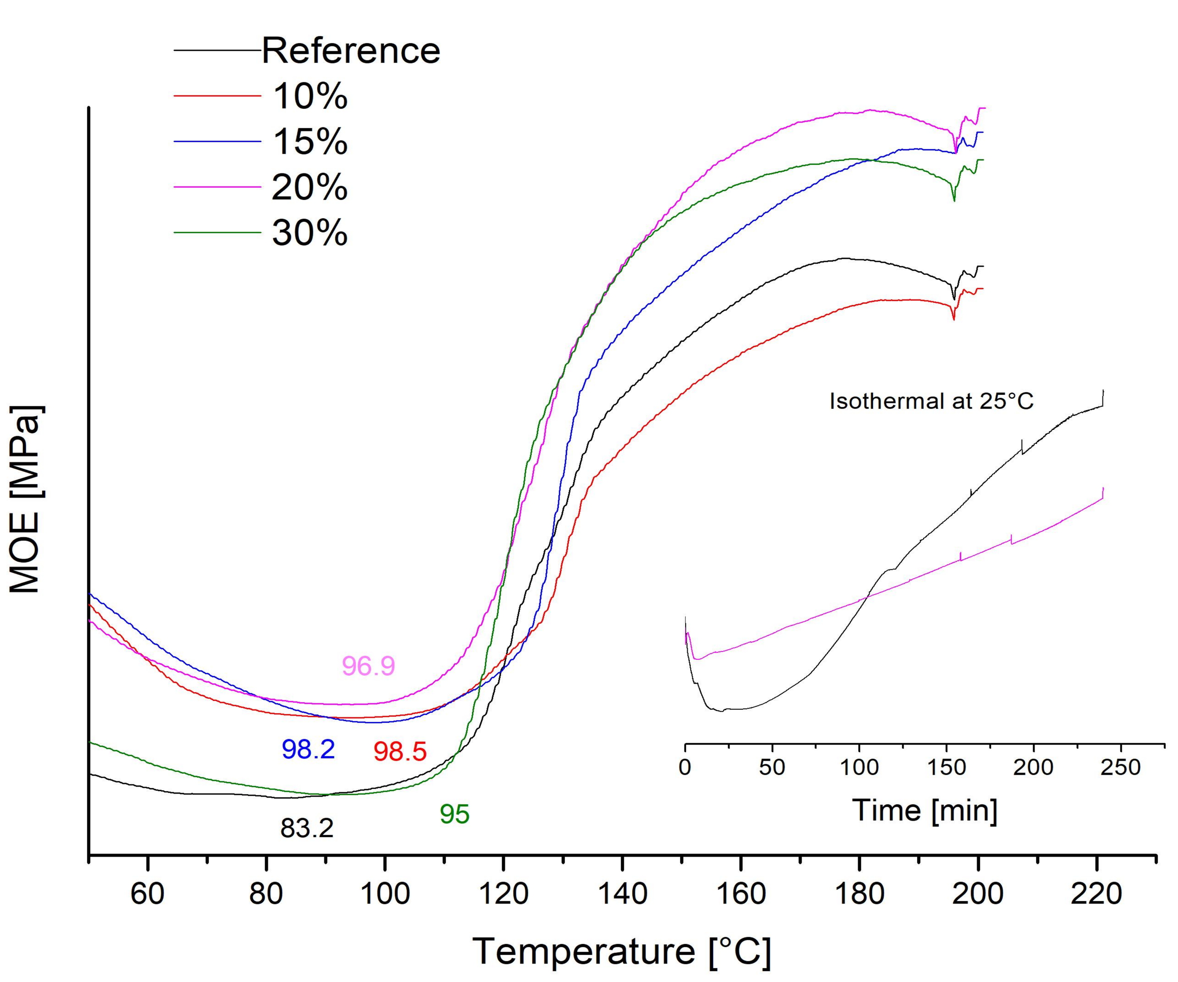

Figure 5. Thermomechanical behavior of tannin-furanic resins in comparison with the reference solution.

Thermomechanical analysis:

Non isothermal test (25°C-200°C)

- The addition of the SF leads to an increase in the starting reaction temperature.
- Increasing the SF amount also increase the MOE, showing enhanced properties at 20 wt% content.

Isothermal test at 25°C

- The reaction takes place at room temperature for both resins (reference and with 20%wt of fibroin).
- Slower kinetics (minor slope) is highlighted with fibroin addition. The reaction does not finish until 240 minutes.

Spectroscopic investigations

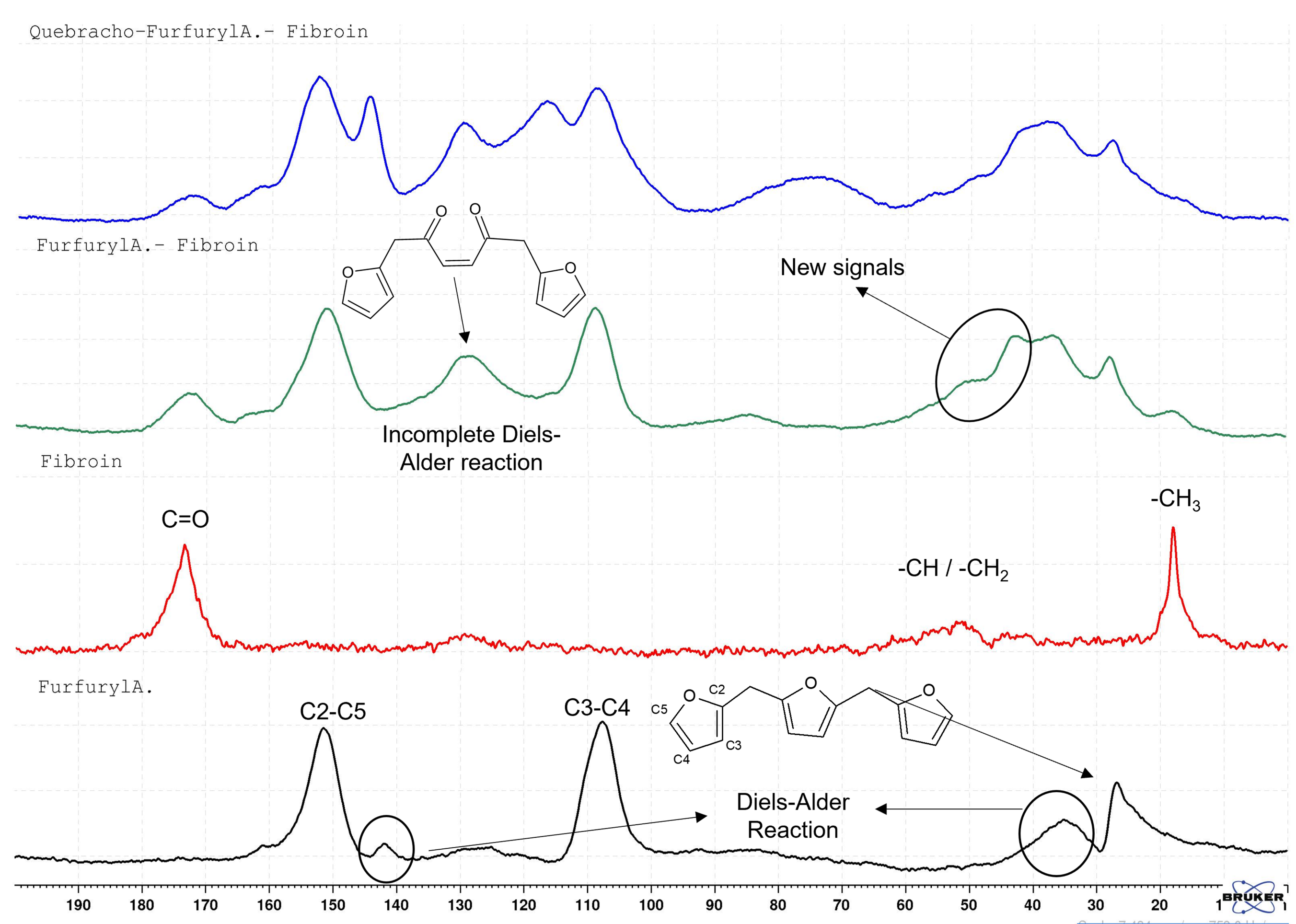

Figure 6. ^{13}C NMR spectra of: furfuryl alcohol (black), silk fibroin (red), furfuryl alcohol-silk fibroin (green), quebracho-furfuryl alcohol-silk fibroin (blue).

Mechanical properties of three-layer plywood

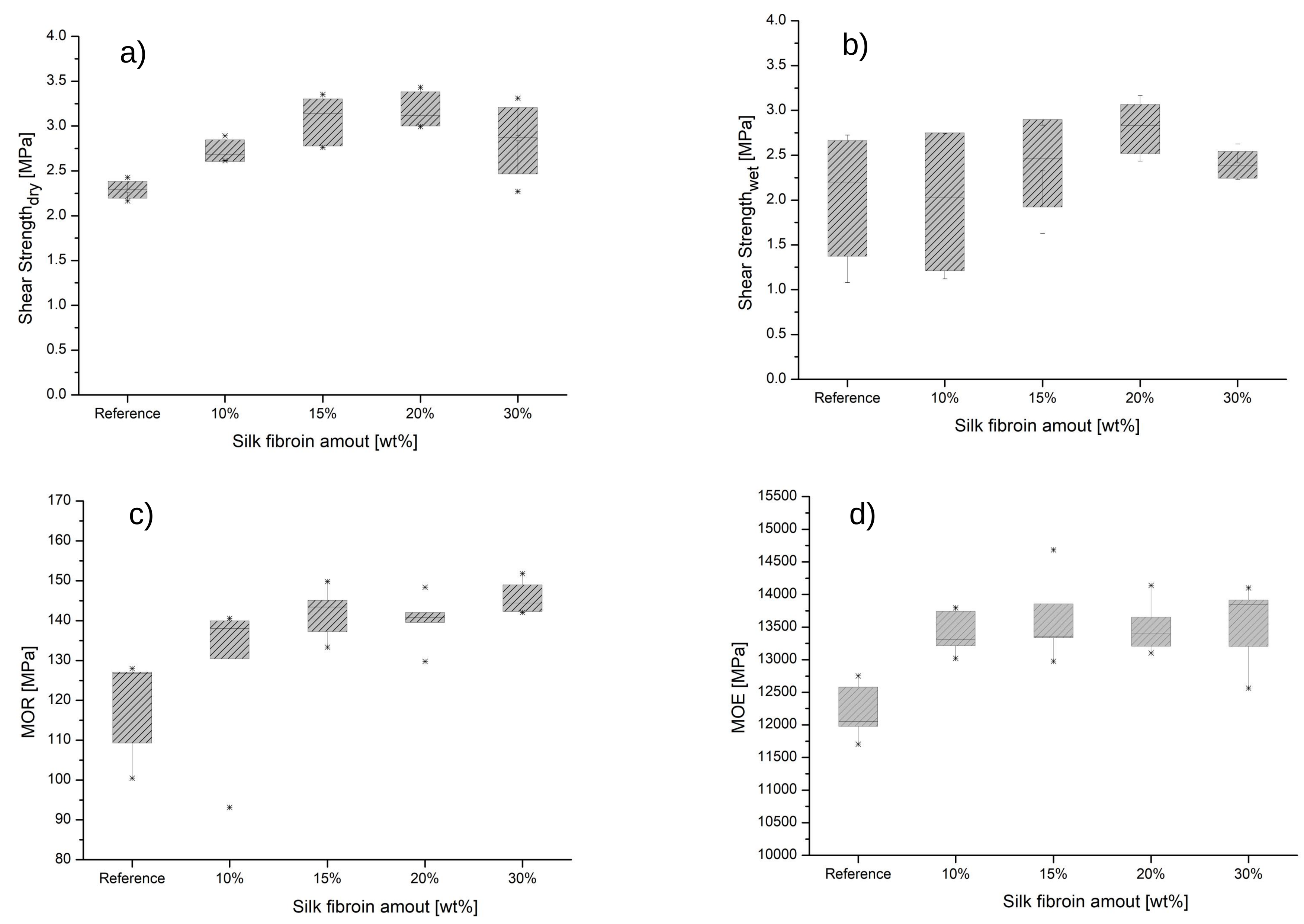

Figure 7. Mechanical properties of 3-layer plywood boards in terms of: Shear strength in dry (SS, a) and wet environment (SS, b), modulus of rupture (MOR, c) and modulus of elasticity (MOE, d).

Mechanical properties of plywood:

Shear Strength (SS)

- The addition of fibroin showed a positive effect on SS $_{dry}$, reporting a significative difference from the reference (p-value < 0.05). The highest values (3.4 MPa) were registered for panels pressed at 20% of fibroin.
- The SS $_{wet}$ is positive affected by the fibroin addition, showing the highest values (2.9 MPa) still at 20% of protein.

Modulus of rupture (MOR)

- A significative difference (p-value < 0.05) between reference panels and other samples was highlighted, while the increase of fibroin did not lead a significative improvement on MOR.

Modulus of elasticity (MOE)

- A significative difference (p-value < 0.05) between reference and samples added with fibroin was highlighted with an increase from around 12200 to over 13500 MPa.

Conclusions

The addition of protein counterpart to furanic-tannin based adhesive leads to:

- Enhanced workability of the adhesive solutions, as depicted in the figure 4.
- Control the furfuryl alcohol-tannin copolymerization in acid environment, extending the polymerization time.
- Speed reduction of the polymerization, confirmed by the presence of diene not involved in Diels-Alder reaction (130-120 ppm), which could be due fibroin-furfuryl A. interactions (new ^{13}C NMR signals at 50-40 ppm).
- Increase the mechanical properties (SS $_{dry\ /\ wet}$, MOR and MOE) of 3-layer plywood glued with tannin-silk formulations. The optimal results were registered with 20% of fibroin content.

References

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