Harakeke Reinforced Furan Bio-Composites

CENTRE FOR ADVANCED MATERIALS MANUFACTURING & DESIGN

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Introduction

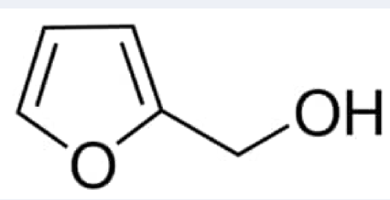
The rising importance of factoring sustainability into the use of composite materials has seen an immense upsurge in the popularity of natural fibre reinforced polymers (NFRP). Both industry and academia have investigated their potential uses for non-structural to semi-structural applications. However, the current dependence on petroleum-based thermosetting polymers, such as epoxies, detracts from the attractiveness and sustainability of these materials. Additionally, there is a great benefit in 'carbon-mile' by using locally cultivated natural fibres rather than imported materials grown and processed overseas. This research project studied the potential of a fully bio-based composite material relying on New Zealand native harakeke (Phormium Tenax) fibres for the reinforcement of a polyfurfuryl alcohol matrix.

Within this work constituent materials have been processed and mechanically characterized. Processing has included the resinification of monomeric furfuryl alcohol and the alkaline treatment of mechanically processed harakeke fibres. Manufacturing methods for producing high quality long-fibre composites have been developed; incorporating partially cured polyfurfuryl alcohol in a compression moulding process. Mechanical performance has been determined, along with durability. These properties have been benchmarked against traditional NFRPs relying on petrochemical thermosetting polymer matrices. This work quantifies the feasibility of using local grown harakeke fibres in a fully bio-derived high-performance composite.

Figure 1: Harakeke (Phormium Tenax) grown in coastal New Zealand environment [1]

Figure 2: Raw Harakeke (Phormium Tenax) fibres

Constitutive Materials



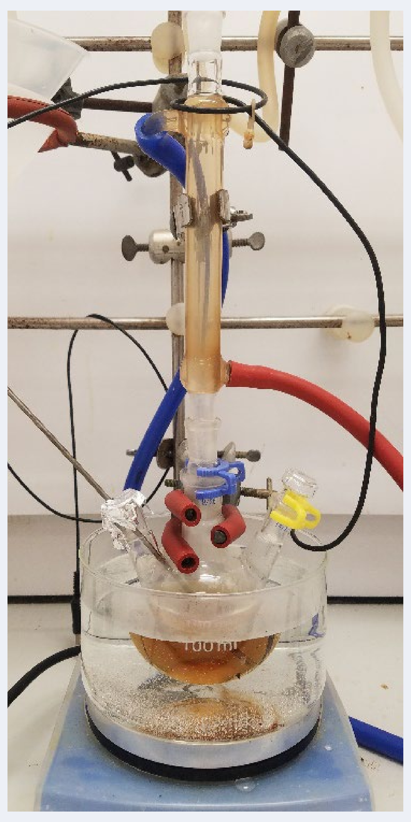


Figure 3: Gradual acid catalysed polymerisation of furfuryl alcohol

'Furan Resin' was prepared by the gradual acid catalysed polymerisation, using furfuryl alcohol and p-toluene sulfonic acid [2]. Cure characteristics were investigated through DSC with catalyst and cure temperatures selected to be compatible with natural fibres and compression moulding.

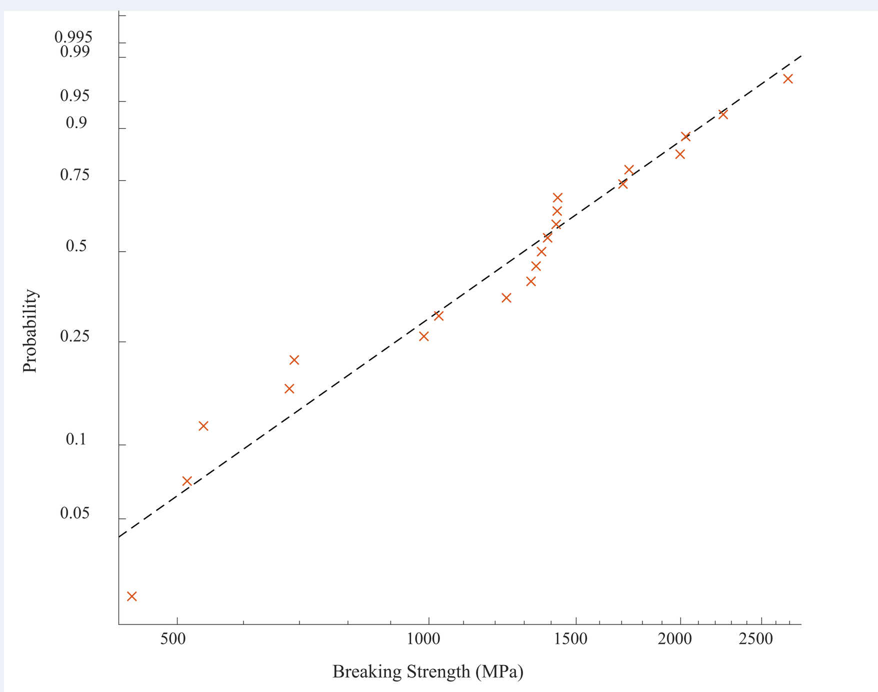
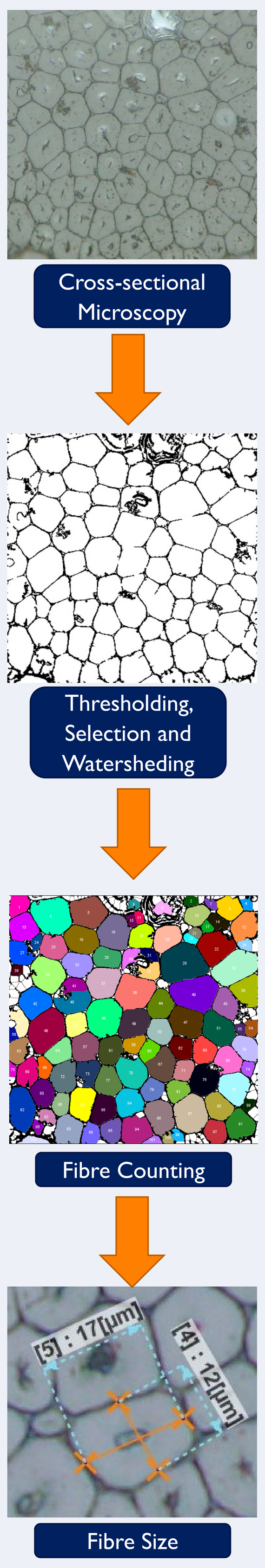


Figure 4: Fibre Strength Weibull Probability Plot



Harakeke fibres have been characterised to determine the; density using a gas-pycnometer, size using image analysis of cross-sectional microscopy (results are presented as equivalent circular diameter), and fibre modulus, strength and failure strain based on ASTM C1557-14.

Density	**1.46 g/cm³** (13.9% COV)
Size	**7.56 μm** (28.3% COV)
Tensile Modulus	**24.3 GPa** (37.6% COV)
Tensile Strength	**1343.17 MPa** (44.3% COV)
Failure Strain	**6.0%** (43.7% COV)

Composite Manufacture

Composite specimens were produced from quasi-aligned harakeke long-fibres. The fibres were impregnated by hand with the prepared catalysed furan resin before being laid into an aluminium mould. A two-step curing process is then undertaken, firstly a beta-staging at an elevated temperature, then a full hot-press consolidation for final cure.

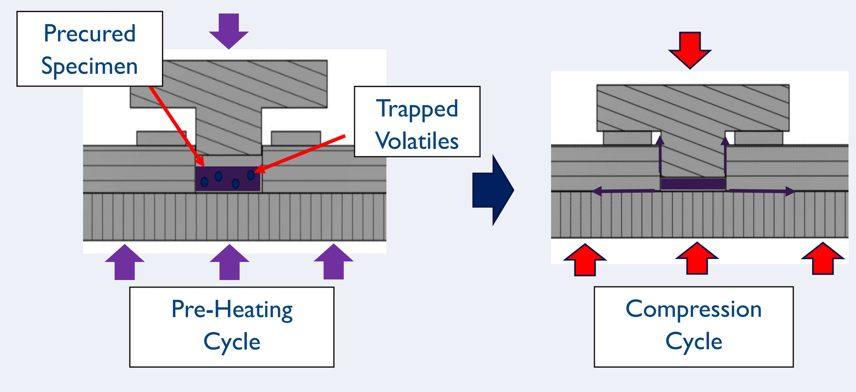
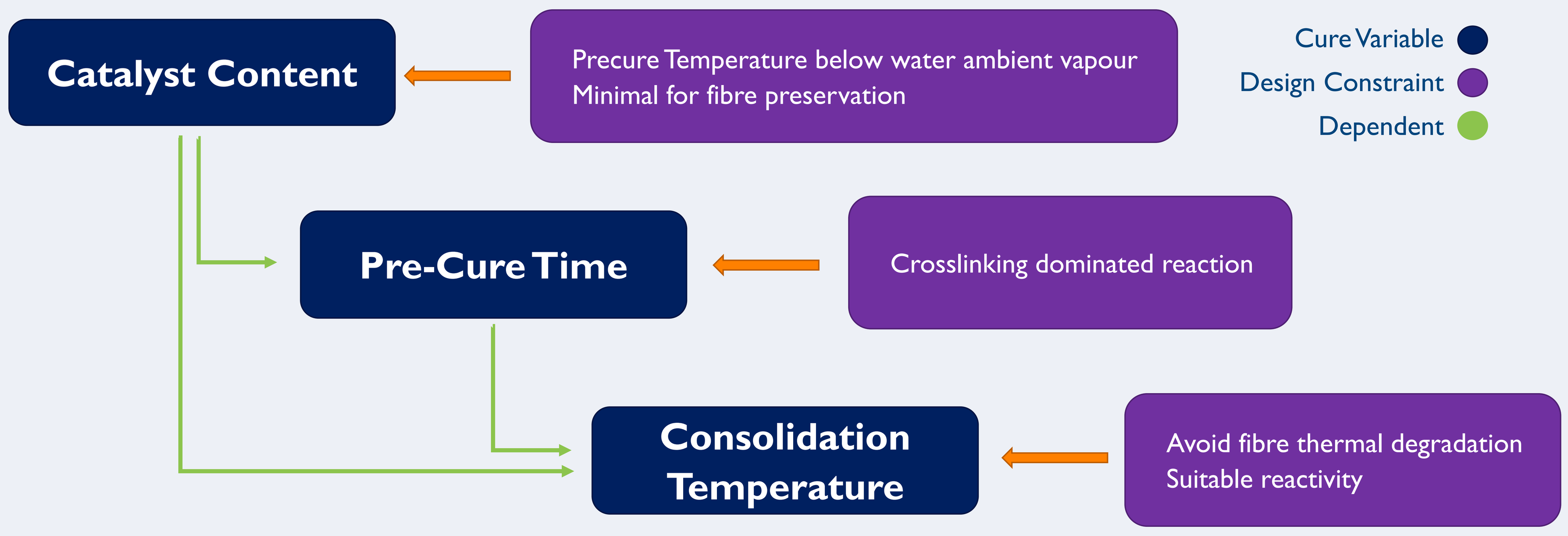


Figure 5: Illustration of composite moulding process



Composite manufacturing quality such as void content, fibre dispersion, and wetting were investigated via cross-sectional microscopy, as well as the was effects of the duration of each stage of curing and fibre volume ratio.

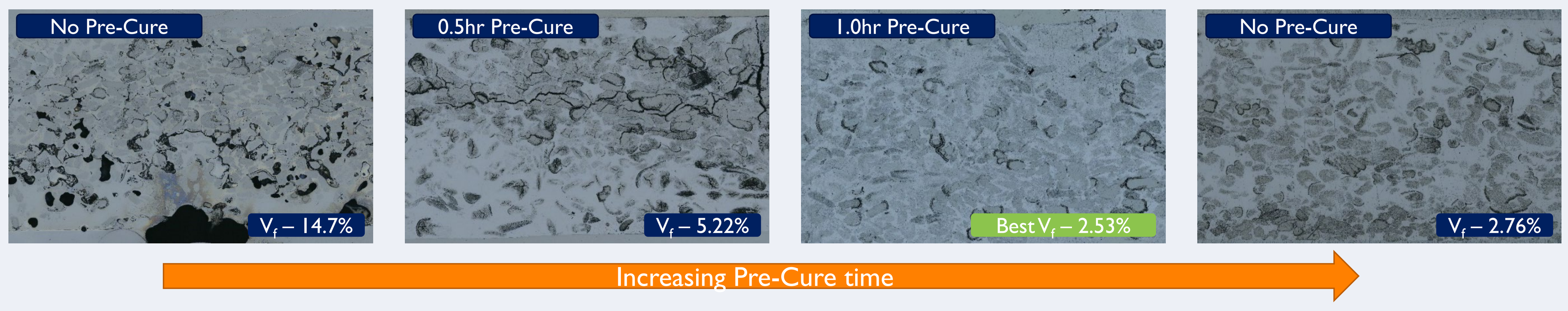


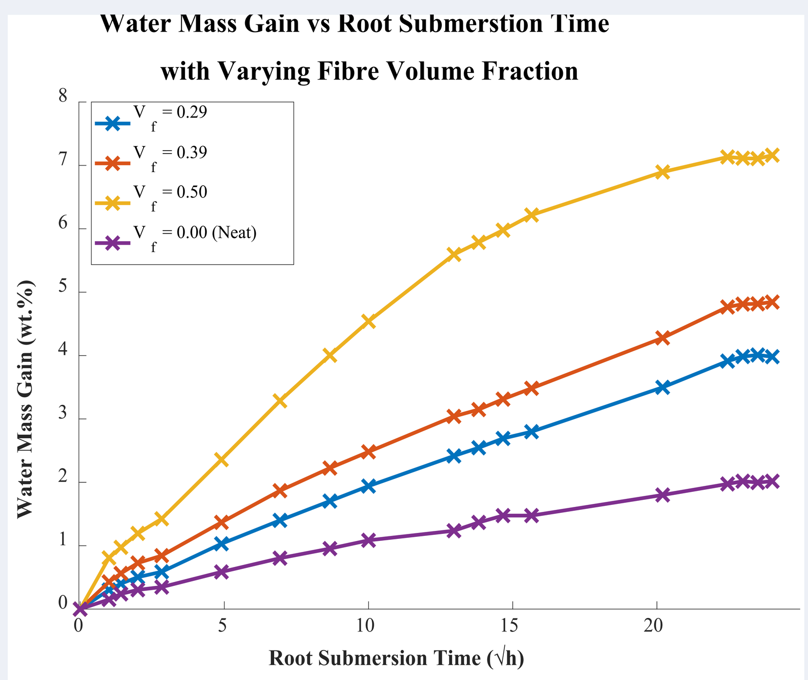
Figure 6: Cross-sectional microscopy imaging indicating the correlation between pre-cure time and void fraction

Environmental Durability

Composite moisture uptake with time has been assessed and correlated with increases in fibre volume fraction. Composite specimens were submerged and mass recorded over an approximately one month period.

Preliminary composite flammability was undertaken via vertical burn testing. Clear signs of fibre pyrolysis and some signs of matrix degradation were evident.

Figure 7: Water absorption of composite specimens



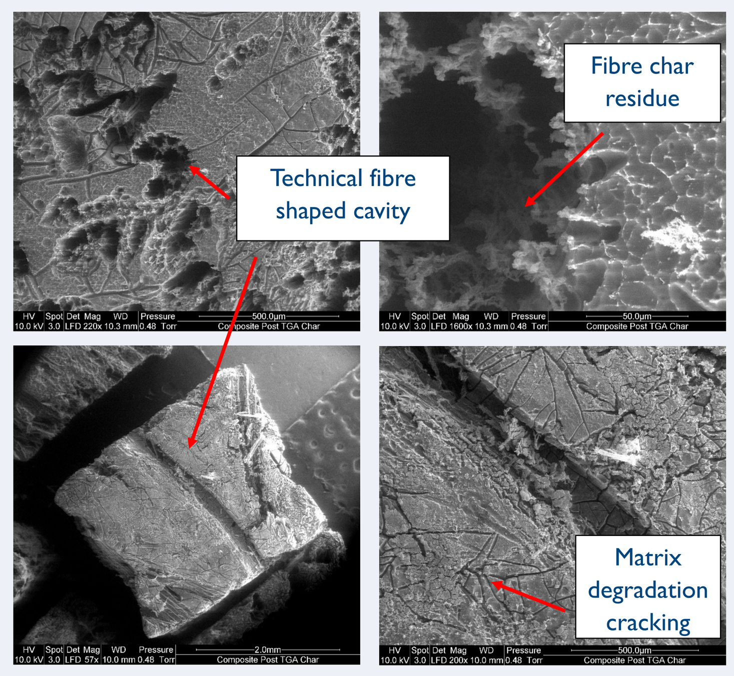


Figure 8: SEM images of composite post flammability testing

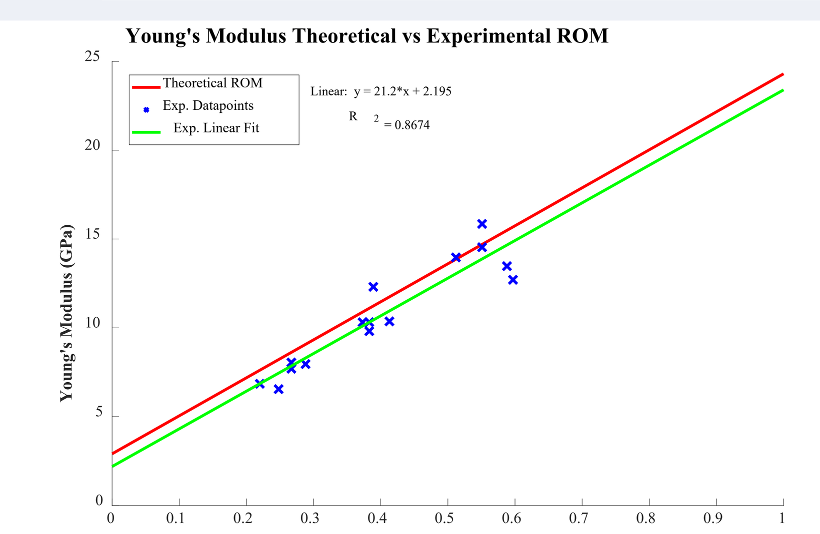
Mechanical Performance

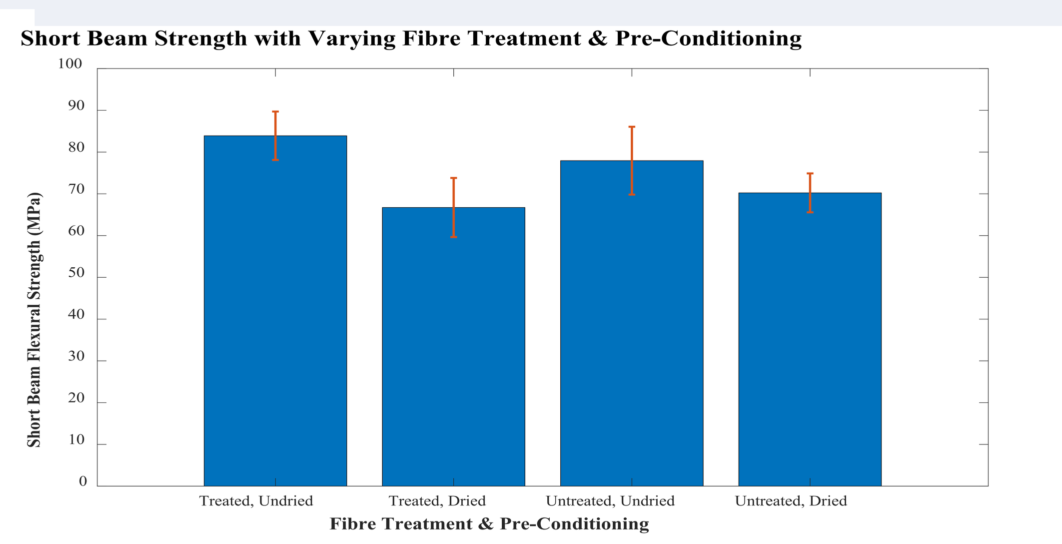
Resulting tensile [3] and short-beam [4] mechanical properties have been assessed. Youngs's modulus is shown to follow ROM predictions, while failure strain, and therefore strength, appears to be dominated by the low-elongation polyfurfuryl alcohol .

V_f (%)	E_t (GPa)	σ_{cr} (MPa)	ε_{cr} (%)
26	7.42 (0.68)	19.29 (7.01)	0.26 (0.10)
39	10.62 (0.89)	24.70 (4.85)	0.23 (0.06)
55	14.11 (1.06)	33.88 (3.83)	0.24 (0.05)

No statistical difference has been observed in short-beam strength for treated vs untreated fibres. Undried fibres appear to have a statistically higher short-beam strength, potentially as a result of the condensation polymerisation that occurs during cure.

Short beam strengths	σ_{cr} (MPa)
Treated-Undried	83.90 (11.60)
Treated-Dried	66.73 (14.14)
Untreated-Undried	77.94 (16.25)
Untreated-Dried	70.23 (9.32)





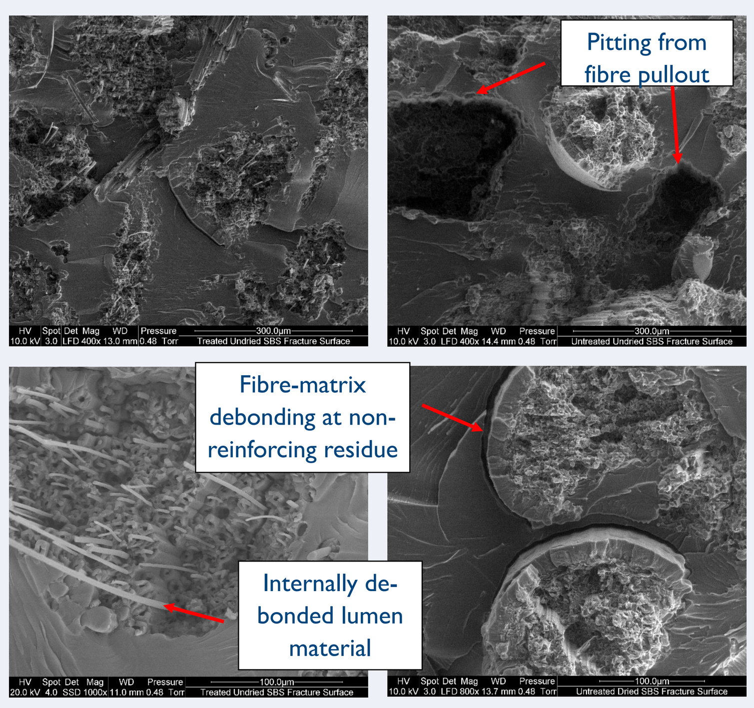


Figure 9: Fracture surface SEM demonstrating fibre-matrix interfacial separation and internally filled fibres

SEM-based fractography has indicated fibre-matrix interface common location of failure initiation. Also an indication there is potential infiltration of the Furan Resin into the lumen of the fibres.

Acknowledgements and References

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[2]: C. C. M Ma, M. S. Yn, J. L. Han, C. J. Chang, and H. D. Wu, (1994) "Pultruded fibre-reinforced furfuryl alcohol resin composites: I. Process feasibility study,"

[3]: American Society of Testing and Materials. (2014). ASTM D3039-08: Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials.

[4]: American Society of Testing and Materials. (2022). ASTM D2344-22: Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates

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