fibers

MDPI

Quantitative Assessment and Visualisation of the Wood and Poly(Lactic Acid) Interface in Sandwich Laminate Composites

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Supplementary Materials

Fluorescence chromophore label grafting to PLA

The first method employed was solvent-based and involved using a modified literature procedure to react acriflavine and PLA in chloroform solution. PLA polymer was dissolved in chloroform in a round bottom flask. The flask was immersed in an oil bath and heated at the stated temperature while maintaining stirring. In a separate flask, acriflavine (nominally 0.1 % w/w on PLA) was added to water and stirred until the powder was dissolved. Sodium hydroxide (1M) was then added to neutralise the pH to *ca.* pH 8 before the aqueous solution then poured into the chloroform solution to form a heterogeneous reaction mixture. The reaction mixture was heated at either 20, 50, 60 and 70 ˚C and stirred for between 4 and 17 hours. After cooling the solution was separated by either use of a separating funnel or *via* centrifuging. In each case, the chloroform phase was further washed with several portions of water. Water washing was undertaken up to nine times until the washings were deemed colourless and any unreacted acriflavine considered removed from the PLA/chloroform solution. The residual PLA/chloroform solution was then poured onto a foil plate and allowed to evaporate at ambient temperature for at least 24 h. After evaporating the chloroform, the fluorescently labelled PLA was recovered and further dried under vacuum at 45 ˚C for 24 h. This solvent-based method produced final acriflavine loadings on PLA estimated to range from 0.03 % to 0.1 % on PLA as a master-batch.

In a second approach, direct fluorescent labelling of PLA was attempted *via* reactive extrusion using a Haake Rheomix 600 twin screw extruder/mixer coupled with a Polylab OS Rheodrive 7 from Thermo Scientific. Acriflavine grafting to PLA was undertaken by directly mixing acriflavine with PLA at 180 ˚C for 3 mins. This processing temperature

and time was deemed sufficient to allow for the grafting reaction and avoid any significant fluorescence degradation of the chromophore.

Initially, to achieve the quality microscopy images produced in this study, an appropriate fluorescence label concentration in poly(lactic acid) (PLA) was required which also matched the inherent autofluorescence intensities of wood components in the softwood and hardwood veneers used. The fluorescent chromophore acriflavine was evaluated over a concentration range of 0.0001 % to 0.01 % in PLA. Practically, higher acriflavine concentrations (>0.05 % w/w) have been developed previously for polyester systems processed as wood-plastic composites]. However, in this current study with wood veneer laminates, the PLA 0.05 % chromophore concentration and lower degree of thermomechanical processing led to undesirably high PLA fluorescence intensity relative to the lignin autofluorescence]. To improve upon acriflavine grafting efficiency to PLA and better anticipate thermal degradation of the fluorescence chromophore, the fluorescence labelling of PLA was reinvestigated using amido-functionalisation *via* solvent or reactive extrusion processing. This revealed acriflavine could be grafted to PLA by amide formation variously along the polyester backbone via de-esterification. A temperature >60 ˚C and reaction time exceeding 16 h was satisfactory to graft acriflavine to PLA. A maximum temperature of 70 ˚C was favoured to ensure the acriflavine fluorescence intensity was not compromised. Coupled with efficient washing, master-batches of fluorescently labelled PLA could be readily produced. Lower temperatures (<50 ˚C) and shorter reaction time (<9 h) led to significant unreacted acriflavine isolated on washing or centrifuging the PLA reaction solution. Analysis also revealed no significant PLA hydrolysis via polymer de-estification and cleavage. Results showed PLA molecular weight was similar after 7 h and 17 h at 63 ˚C with acriflavine incorporation in PLA approximated at *ca.* 0.07 % at both reaction times using an initial amount of 0.1 %.

Table SM1. General Confocal Microscope settings used to obtain the CLSM images.

Configuration	Argon laser: 20 % power DPSS 561 laser
Acquisition	
Scanning mode: xyz	Speed: 400 Hz
Resolution: 1024 x 1024 pixels	Pinhole: 1.5 AU
Stepsize: 2-3.5 μm	
Excitation wavelengths: 476 nm at 50 %	561 nm at 32 % intensity
Detector PMT2 (488-507 nm range)	predominantly the acriflavine fluorescence (as PLA, green)
Detector PMT3 (570-707 nm range)	employed to detect lignin fluorescence within the wood (red).

Table SM2. Comparisons of tensile bond strength for veneer composites produced with maple and spruce veneers and with 5-25 % wood fibre content in PLA foils.

Sample PLA/MDF	Pressing Temperature (°C)	Average Bond strength, (N/mm²) n = 8-10			
		Maple		Spruce	
		Average	Std. Dev.	Average	Std. Dev.
100/0	140	8.69	1.03	4.67	0.86
	200	10.42	0.35	5.70	0.85
95/5	140	7.79	1.03	-	-
	200	10.31	0.49	-	-
75/25	140	6.41	0.28	3.49	1.14
	200	9.09	0.79	5.62	0.91

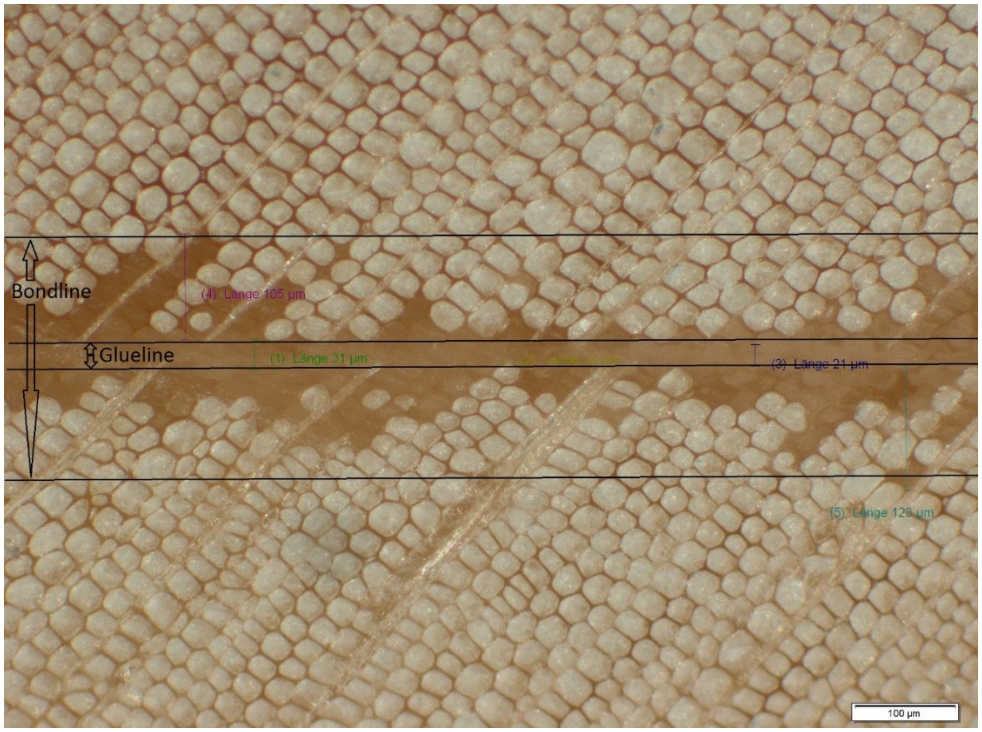

Figure SM1. Schematic describing bondline and glueline distinctions.

Representative Confocal Microscopy Images

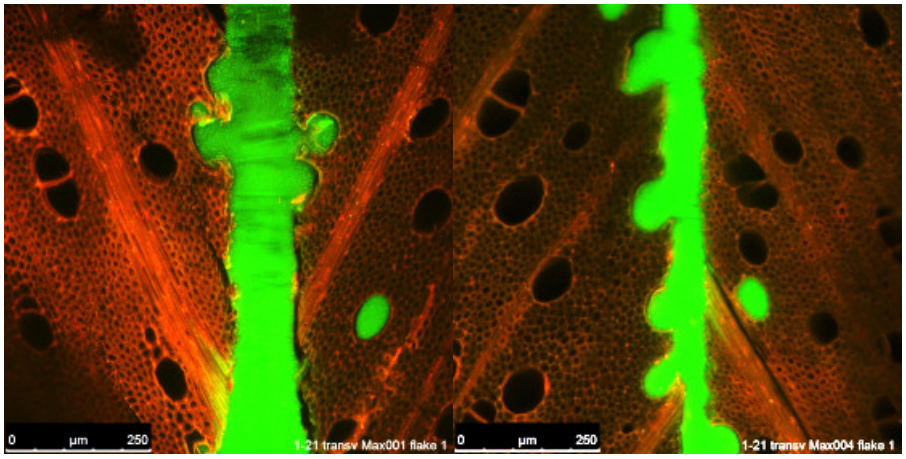

Figure SM2. Maple-140, transverse view.

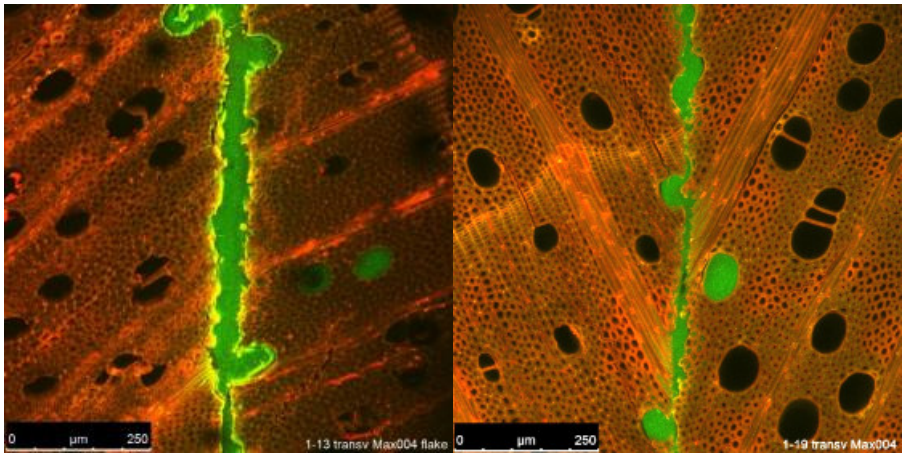

Figure SM3. Maple-200, transverse view.

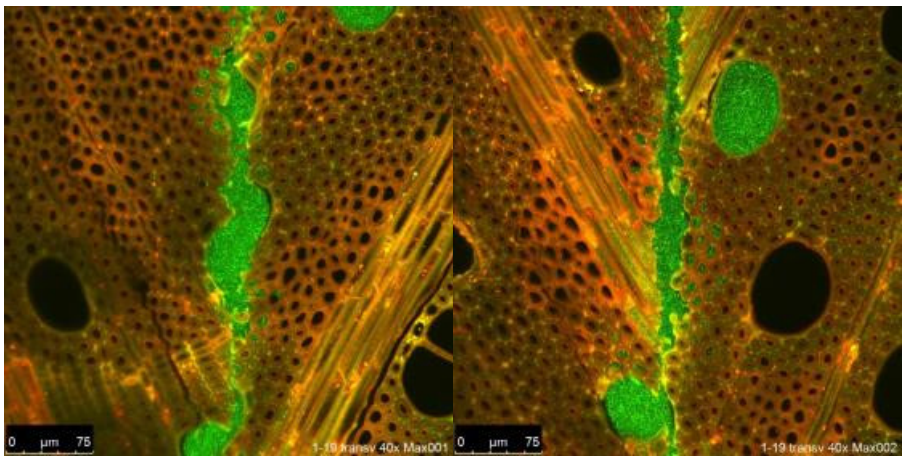

Figure SM4. Maple-200, transverse view at 40x magnification.

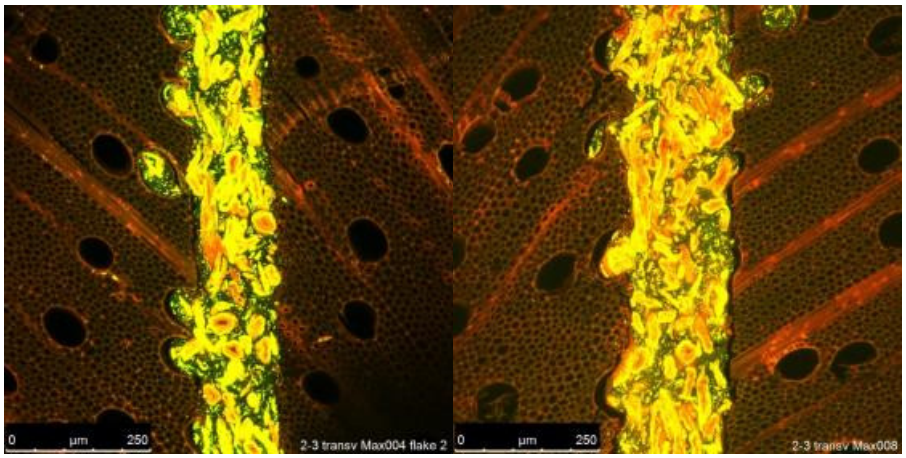

Figure SM5. Maple-140-25MDF, transverse view.

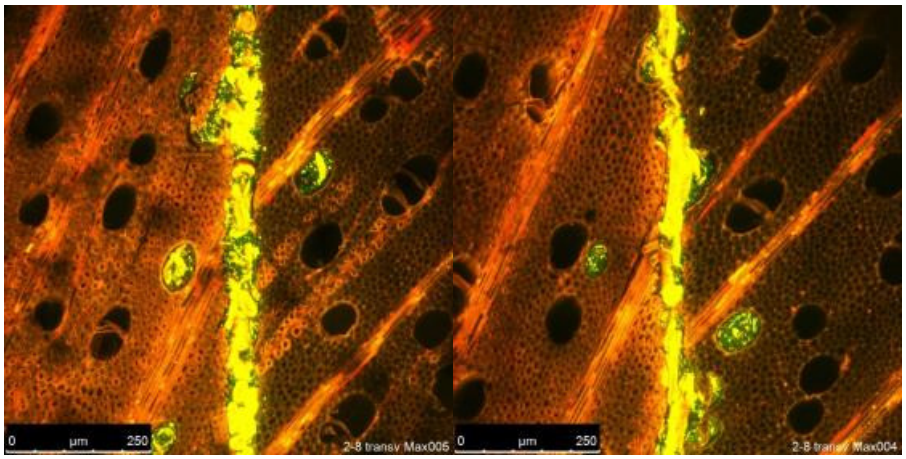

Figure SM6. Maple-200-25MDF, transverse view.

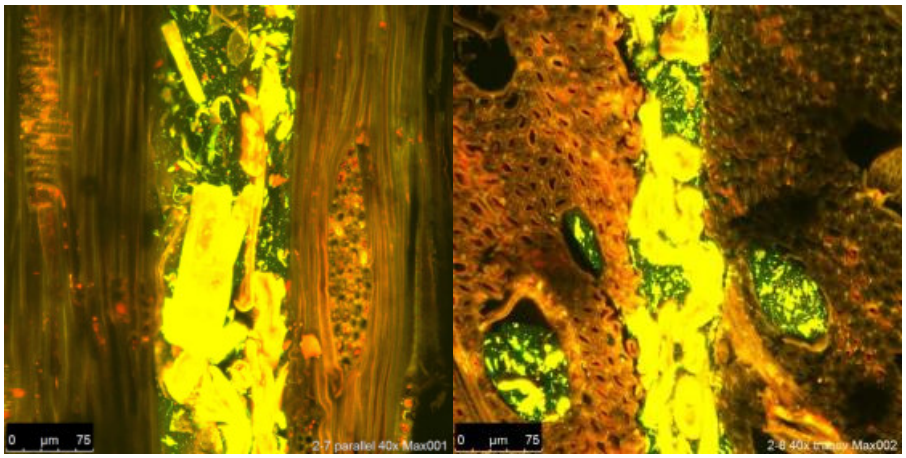

Figure SM7. Maple-200-25MDF, parallel view Figure 39 Maple-200-25MDF, transverse view, 40x magnification.

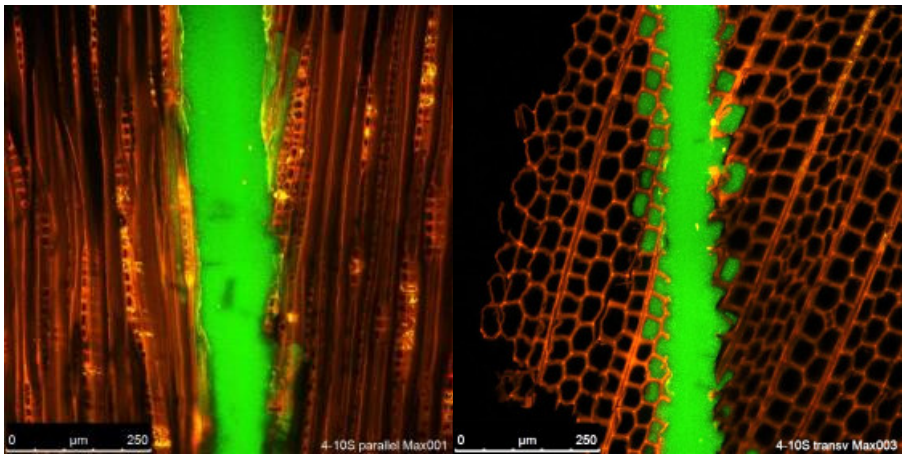

Figure SM8. Spruce-140, parallel view (left) Spruce-140, transverse view (right).

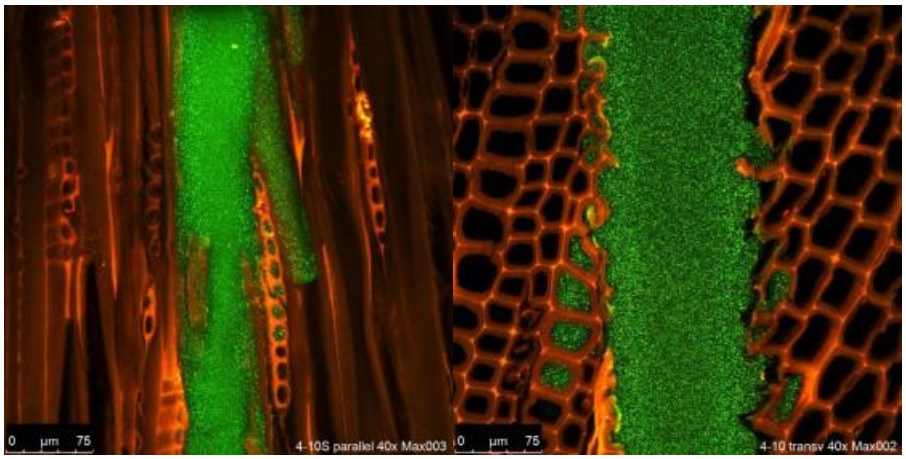

Figure SM9. Spruce-140, parallel (left) and transverse (right) views at 40x magnification.

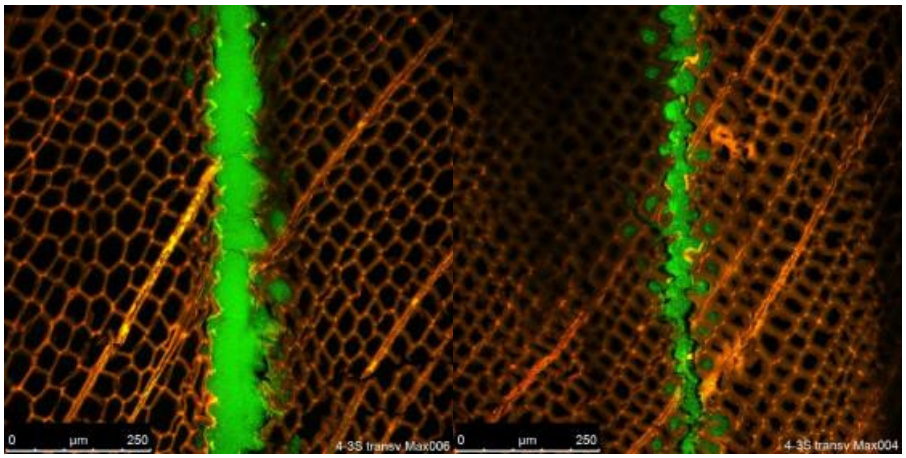

Figure SM10. Spruce-200, transverse view.

Failure Surface Assessments

Qualitative images were obtained for various fracture surfaces after ABES tensile testing. Each composite sandwich sample formed with PLA/Wood Fibre 95/5

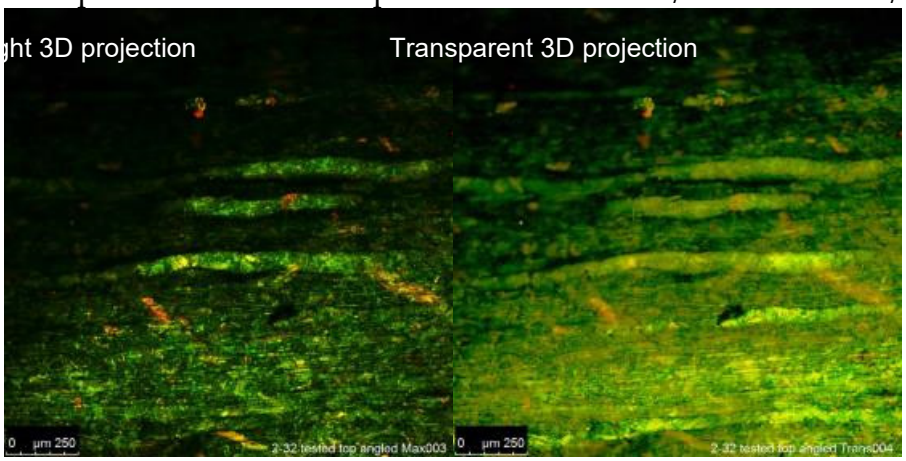

Figure SM11. Sample 2-32 CLSM, PLA side top view.

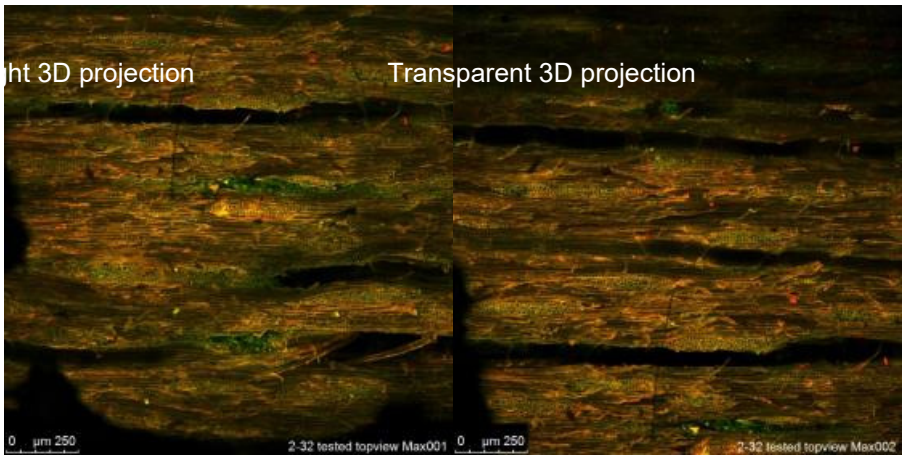

Figure SM12. Sample 2-32 CLSM, veneer side top view.

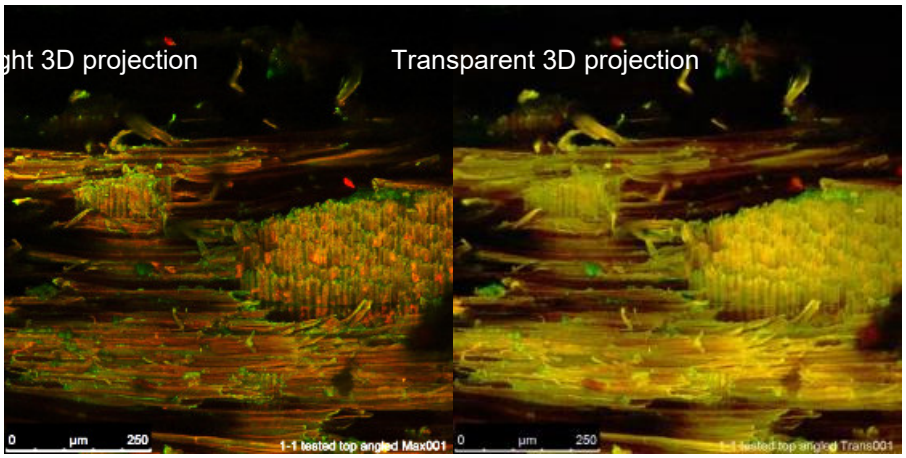

Figure SM13. Sample 1-1 veneer tearing along fibre length.