

## A Natural Flavonoid, Chrysin, Improving Wood Properties *via* Impregnation

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A broader utilization of wood can be achieved by eliminating its drawbacks such as low dimensional stability with changing moisture content and low durability against various bio-organisms. Heartwood formation is nature's solution that functions through biosynthesis and accumulation of some phenolic compounds in the cell walls, leading to more durable and stable wood. In this study, a natural flavonoid molecule, chrysin, was used to improve Scots pine wood properties. Hydrophobic chrysin was impregnated into wood after a pre-treatment. The chrysin modification reduced the water uptake of the wood cell walls by up to 33% and increased the dimensional stability of the Scots pine by up to 30%. Infrared spectroscopic analysis revealed the chemical characterization of the bio-inspired modification. In contrast to the many modification methods that establish covalent bonds between hydroxyl groups of wood polymers, chrysin was bulked into wood cell walls and stabilized by intermolecular interactions.

*Keywords:* Chrysin; Biomimicking; Dimensional stability; Flavonoid; Wood modification

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### INTRODUCTION

Wood has the largest usage among all the engineering materials derived from natural renewable resources, making it economically significant. Its utilization in the furniture and construction fields can be attributed to its excellent mechanical properties, aesthetic appearances, and light weight. However, due to its chemical composition, wood has some negative properties such as low dimensional stability and durability. These limitations restrain further utilization of wood, especially in the outdoor fields (Hill 2006). There are several methods to preserve wood from biological attack; however, most of the conventional preservatives contain toxic metals that cause further issues such as disposal or health problems (Archer and Lebow 2006; Lundholm *et al.* 2007). Chemical modification methods are more ecologically friendly treatments that have been studied for decades as an alternative to metal-based and other wood preservatives (Hill 2006; Rowell 2012). Acetylation, furfurylation, and DMDHEU are some established and commercialized treatments frequently used in wood products (Hill 2006). Chemical modification establishes new covalent bonds between the impregnated chemicals and hydroxyl groups of cell wall polymers such as cellulose, hemicelluloses, and lignin (Hill and Jones 1996; Hill 2006; Rowell 2006), or it bulks the micro/nano voids of the cell walls (Ermeydan *et al.* 2012; Kohlmayr *et al.* 2013; Sandberg *et al.* 2017).

Recently, a biomimetic approach to improve the water repellency and dimensional stability of wood has been studied (Ermeydan *et al.* 2012). This bio-inspired modification mimics heartwood formation in flavonoid generating wood species, such as black locust

(*Robinia pseudoacacia*) (Smith *et al.* 1989), oak (*Quercus hartwissiana*) (Ucar and Ucar 2011), and cedar (*Juniperus virginiana*) (Kirker *et al.* 2013). The heartwood in these species contains high amounts of extractive flavonoid molecules, which strongly affect several characteristics of wood, such as color, odor, durability, and dimensional stability (Smith *et al.* 1989; Lourenço *et al.* 2010; Latorraca *et al.* 2011). Ermeydan *et al.* (2012) inserted synthetic and hydrophobic 3-hydroxy flavone molecule inside Norway spruce cell walls after a pre-treatment. Unlike some previous studies (Sakai *et al.* 1999), Ermeydan *et al.* (2012) was able to fix flavonoid in the cell wall against water leaching and improved some wood properties (notably water repellency and dimensional stability). As noted, 3-hydroxy flavone is a synthetic flavonoid, and use of a natural polycyclic flavonoid as a wood modifier has not yet been successfully loaded in wood cell walls. The basic advantage of such bio-inspired modification method is having the potential to be a green solution for improving wood properties (Burgert *et al.* 2016).

In this study, water repellency and the dimensional stability properties of Scots pine wood were improved using a bioinspired approach. Scots pine is known for its availability and commercial value, but it is also not very durable and dimensionally instable wood species at outdoor usage. By inserting a natural hydrophobic flavonoid into pre-treated wood, an environmental solution is revealed to improve service life of non-durable wood species.

## EXPERIMENTAL

### Materials

Tosyl chloride (p-toluene sulfonyl chloride), pyridine (98%), acetone (99.5%), and chrysin or 5,7-dihydroxyflavone (98%) were purchased from Sigma (St. Louis, MO, USA) and used as delivered. Scots pine samples with dimensions of 3 x 0.5 x 1.5 cm (L x T x R) and 5 x 5 x 0.5 cm (L x T x R) were used for modification and performance analysis.

### Methods

#### *Tosylation*

Wood samples were pre-treated with tosyl chloride before chrysin modification. For tosylation, 20 samples were first soaked in 200 mL of pyridine in a 1 L reaction flask, then a 760 mmHg vacuum was applied for 45 min. Samples were kept in the pyridine overnight to improve swelling. The pyridine was rinsed, and 200 mL of fresh pyridine was placed in the flask. Tosyl chloride was added, and the reaction was carried out at 5 °C for 18 h. The amount of tosyl chloride (molar mass: 190.65 g/mol) added to the flask was calculated as one equivalent of TsCl per OH functionality in wood (n(OH), calculated as anhydrous glucopyranose equivalent, AGU, molar mass: 162 g mol<sup>-1</sup>).

#### *Impregnation of chrysin*

First, 3 g of chrysin was dissolved in a mixture of solvents (225 mL of acetone, 10 mL of ethanol, 10 mL of distilled water) at 40 °C. After the tosylation reaction, samples were washed with a fresh portion of pyridine once and pyridine was poured out to remove unreacted tosyl chloride or reaction residues. Then, chrysin solution was poured onto the pre-treated samples in the same flask. Pre-treated wood samples were kept in the chrysin solution to let chrysin diffuse into wood, and wood samples in chrysin solution was mixed gently with a magnetic stirrer at 50 °C to evaporate solvent with control in 18 h. After

solvent mixture was evaporated, samples were then washed with several portions of distilled water for 24 h. Later, samples were dried in an oven at 65 °C. The dry weight and dimensions of the modified wood samples were recorded.

#### *Preparation of solvent control samples*

To evaluate the solvent system's effect on the modification process and on performance of the wood material, pyridine+acetone solvent control samples were prepared without using any chemical reagents, tosyl chloride, or chrysin. Samples were first soaked in pyridine, then in acetone, followed by evaporation in accordance with chrysin modification.

#### *Swelling coefficient (S), anti-swelling efficiency (ASE), and water uptake (WU)*

Samples were placed into a bottle filled with distilled water and shaken moderately for 5 days. The wet state weights and sample dimensions were measured. Subsequently, the samples were dried in an oven at 103 °C, and again weights and dimensions were recorded (first immersion cycle). A second cycle of water immersion and drying was carried out with the samples' weights and dimensions for both wet and dry states recorded (second cycle). The swelling coefficient (S), anti-swelling efficiency (ASE), water uptake, and mass loss during the water immersion cycles were calculated as reported (Rowell and Ellis 1978).

#### *Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy*

FTIR was used to determine the chemical changes and composition of the modified samples. The FTIR spectra were measured by an ATR detector on a Bruker Tensor 37 device (Ettlingen, Germany) with a resolution of 4 cm<sup>-1</sup>, between wavenumbers of 4000 cm<sup>-1</sup> and 400 cm<sup>-1</sup>. An average of 32 scans was used as a spectrum for powdered wood samples. OPUS software (Bruker Optik GmbH, Ettlingen, Germany) was used for baseline corrections and smoothing of the spectra.

#### *Scanning electron microscopy (SEM)*

Morphological details of the chrysin modified and reference wood samples were analyzed using a SEM device (Quanta 200 FEG, FEI Instruments, USA) with a large field detector (LFD) operated at 10 kV with a 8-10 mm sample–detector distance and 3.0 nm spot size.

## RESULTS AND DISCUSSION

### Wood Modification Process

Tosylation pre-treatment provides binding of tosyl groups to wood cell wall polymers (cellulose, hemicellulose, and lignin) thorough ester bonds (Chen 1991). This pre-treatment increases the hydrophobicity of wood by shielding hydroxyl groups and promotes further impregnation of hydrophobic molecules in the second step (Ermeýdan *et al.* 2012, 2014). The advantage of bulking wood cell walls with a hydrophobic molecule eliminates the leaching problems of water-soluble reagents, which may improve the outdoor utilization of wood. After tosylation pre-treatment, in the second step, wood was impregnated with chrysin. Chrysin was dissolved in acetone/ethanol/water; the swelling ability of this mixture is quite limited compared with pyridine (Mantanis *et al.* 1994). When

the chrysin solution was poured onto wood swelled with pyridine, the wood cell walls probably shrunk due to the solvent exchange, and chrysin molecules were trapped inside wood cell wall structure.

**Table 1.** Weight Percent Gains and Volume Changes of Scots Pine Wood Blocks after Tosylation and Chrysin Impregnation

Pyridine+acetone (solvent control)		Tosylation		After chrysin impregnation	
WPG (%)	Vol. change (%)	WPG (%)	Vol. change (%)	WPG (%)	Vol. change (%)
-1.4(±0.7)	1.3(±0.7)	7.4 (±0.5)	4.1(±0.6)	15.1(±1.7)	4.7(±0.5)

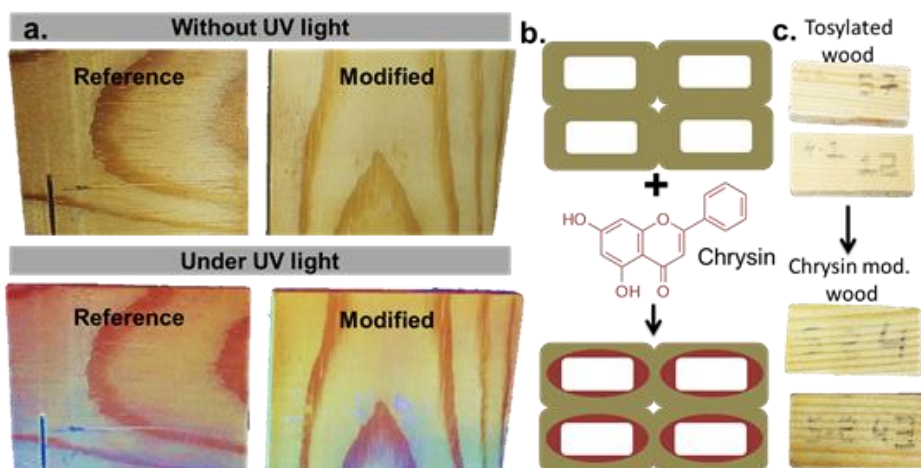
Table 1 shows the weight gains and volume changes calculated for solvent treatment, tosylation, and further chrysin impregnation. Weight gain and dimensional changes after wood modification provide preliminary information about the success of the treatment. The amount of tosyl groups attached to wood polymers has a critical importance for the further impregnation of the hydrophobic molecule (Ermeýdan *et al.* 2014), and 7.4% weight gain is close to the limit for these samples as proven in-house experiments. After chrysin impregnation, the average weight gains of the samples increased up to 15.1%, which means that about 7% weight gain was obtained only from chrysin impregnation. On the other hand, *via* the solvent control system, samples lost about 1% of their weight which may be due to the leaching of some of the extractives or lignin in wood.

As noted, the average weight gain for the tosylation was 7.4%, which is the result of bonding between tosyl groups and free hydroxyl groups in the cell wall polymers. The same molar ratio (1:1) of tosyl chloride to calculated hydroxyl groups was used as reported before by Ermeýdan *et al.* (2012, 2014). However, it was reported that Norway spruce gained 14 to 16% weight using the same tosylation method. This difference, caused by the same methods, is probably due to the sample shapes, which were 3x1.5x 0.5 (LxRxT) cm for this study and 0.5x1.0x1.0 (LxRxT) cm for the earlier studies. The reactivity and yield of wood modifying reactions are related to the availability of hydroxyl groups (Hon 1996) and having larger transverse-section (Maclean 1960). Thus, having larger cross-section surfaces promotes the entrance of the chemical reagents resulting in higher weight gains for tosylation reaction. In the current study, the cross-sectional area of the sample was smaller, thus the yield of the reaction was smaller.

In addition to weight gain results, volume changes also give valuable information on wood modification (Table 1). Positive changes in volume after modification may be interpreted as modification success because cell walls with loaded molecules have increased volume (Hill *et al.* 2004). The solvent control samples had almost no volume changes, but dissolution of the cell wall polymers and further chemical re-structuring created a slight increase (1%). However, tosylation pre-treatment created about a 4% volume increase, where chrysin addition increased volume up to 4.7%, which implies that chrysin may enter inside wood cell walls.

Chrysin is a natural flavone that can be extracted from various sources, such as propolis and honey (Gambelunghé *et al.* 2003), and one of the characteristic properties of flavonoids is an ability to reflect UV light (Saewan and Jimtaisong 2013). In Fig. 1a, chrysin modified samples are shown under UV light and compared with untreated Scots pine. The chrysin modified samples had a yellowish color under UV light. This finding

also correlates with the previous studies (Ermeýdan *et al.* 2012) that show the ability of UV reflection of flavonoid type molecules.

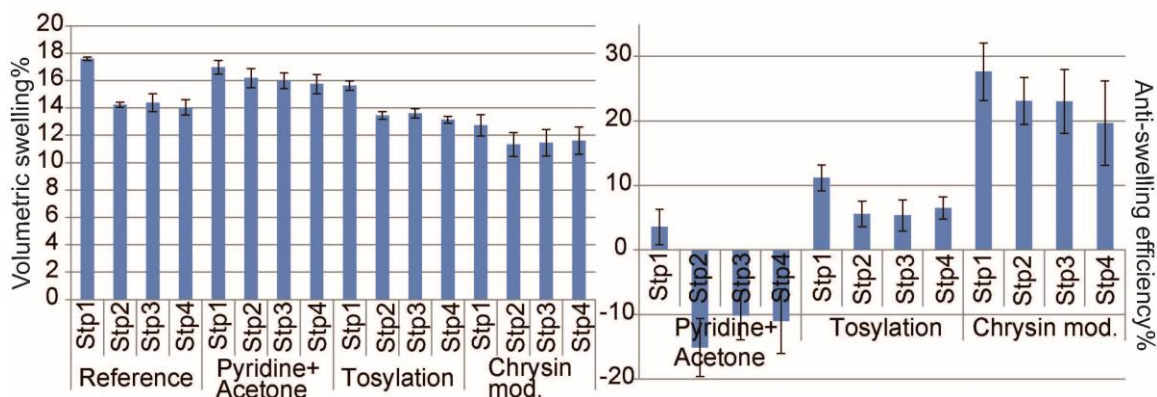


**Fig. 1.** a. Untreated and treated samples shown with/without UV light b. Schematic representation of cell wall modification c. Tosylated and chrysin modified samples

### Dimensional Stability

Dimensional stability is one of the key properties that effect the long-term utilization of wood outdoors. With changing humidity, wood swells and shrinks (Fengel and Wegener 1984). Dimensionally stable wood does not swell much, and the heartwood of some species has properties that make it highly qualified wood (Kirker *et al.* 2013). The dimensional stability of wood samples is measured by the method established by Rowell and Banks (1985), which includes water soaking and oven drying cycles, from which the swelling coefficient (S) and anti-swelling efficiency (ASE) are calculated. The S and ASE values for the four steps (swelled-dried-swelled-dried) are shown in Fig. 2, where the swelling coefficient is calculated by the volume changes during water soaking and drying cycles, and high swelling implies less dimensional stability. In Fig. 2, Scots pine has an average volumetric swelling of 14.5%, which is similar to the reported data (Ahmed and Morén 2012; Farsi *et al.* 2013), and differences can be accepted as due to natural variability. Solvent control (pyridine+acetone) samples have an average swelling of 16%, which is more than the reference samples due to the leaching of some extractives. On the other hand, tosylation reduced swelling of wood slightly to 13%, where chrysin impregnated wood samples have an average swelling of 11.5%.

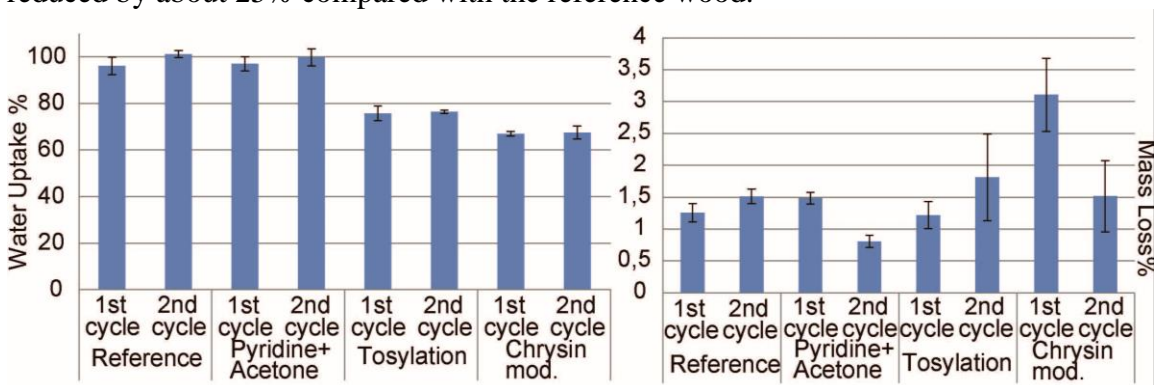
The ASE coefficient checks the modified samples swelling against reference wood, which simply means that high ASE (%) indicates high dimensional stability for the samples. As shown in Fig. 2, the ASE of solvent control (pyridine+acetone) showed negative a ASE value around -10%, indicating that it was worse than the reference Scots pine. In contrast, tosylation provided dimensional stability to the wood (around 5%), which is in accordance with the results (10%) reported before (Ermeýdan *et al.* 2014). The ASE of the chrysin modified wood samples had maximum values around 25%, which indicates a substantial improvement.



**Fig. 2.** Left: Average swelling values of the wood samples. Right: Anti-swelling efficiency values for solvent control, tosylated, and chrysin modified wood

### Water Uptake and Mass Loss Values

In Fig. 3, water uptake of the wood samples was used to evaluate the improvement of water repellency. After the 1<sup>st</sup> and 2<sup>nd</sup> water soaking cycles, reference Scots pine had an uptake of 100% of its dry weight (Can and Sivrikaya 2016). Pyridine+acetone (solvent control) wood samples took the same amount of water as the reference wood. As reported (Ermeydan *et al.* 2012, 2014), tosylation increases the hydrophobicity of wood to some extent *via* its reaction with hydroxyl groups, and water uptake of tosylated samples was reduced by about 25% compared with the reference wood.

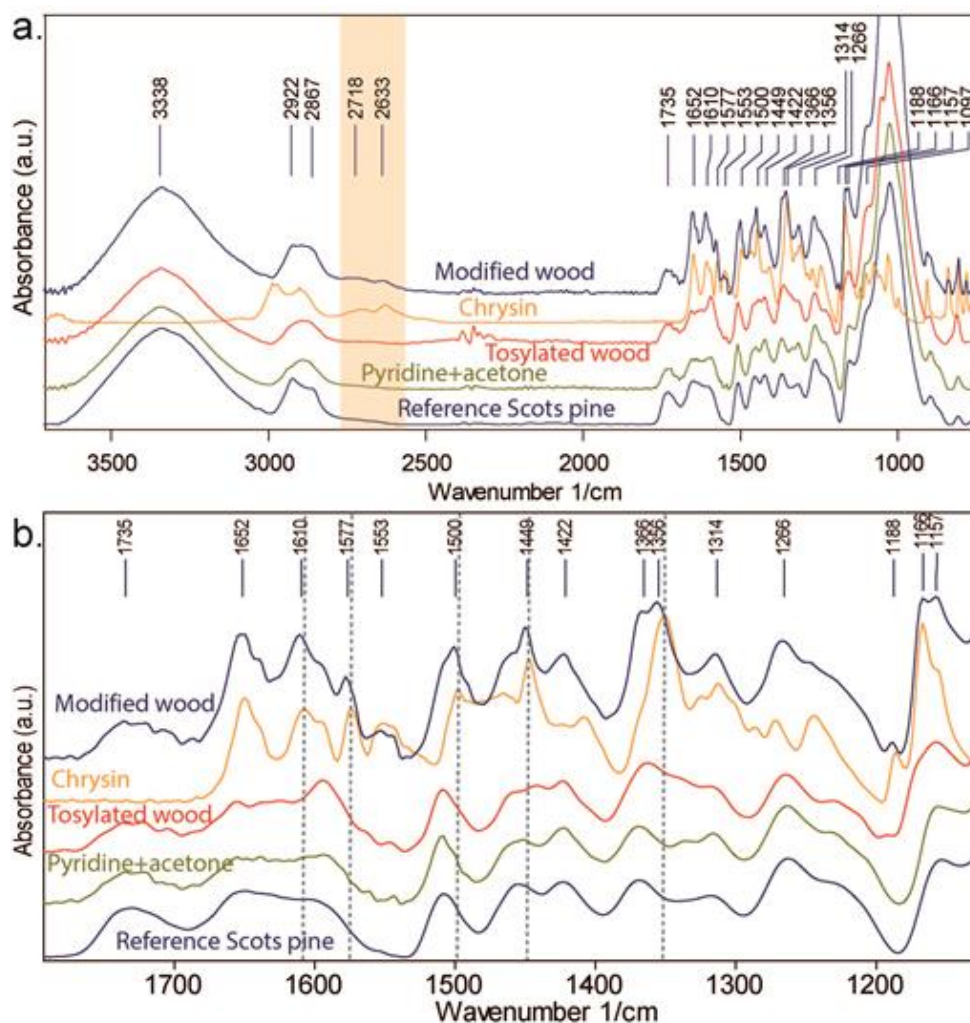


**Fig. 3.** Left: Water uptake values for reference, pyridine+acetone, tosylated, and chrysin modified wood. Right: Mass loss values during water soaking-oven drying cycles of reference, pyridine+acetone, tosylated, and chrysin modified wood samples.

According to the results shown in Fig. 3, chrysin impregnated wood samples improved water repellency up to 33% compared with reference wood, which indicates chrysin addition targets wood cell walls and blocks water entrance more effectively (Hill 2006; Han *et al.* 2018). Chrysin molecules could not be removed by water immersion, which can be interpreted as the establishment of stable interactions between chrysin and cell wall components (Ermeydan *et al.* 2012).

Another parameter that shows the stability of inserted chemicals inside the wood cell wall is the percentage mass loss occurring during water immersion-oven drying cycles. Repeated water soaking-oven drying removed some of the extractives (in total about 3%) from reference Scots pine, as shown in Fig. 3. There was no significant difference between the mass losses of the reference, pyridine+acetone, or tosylation samples. However,

chrysin modified samples lost around 4.5% of their total mass, which was slightly higher than the reference wood. This mass loss in chrysin modified samples, especially in cycle 1, may be explained by the leaching of chrysin molecules left in the lumina.



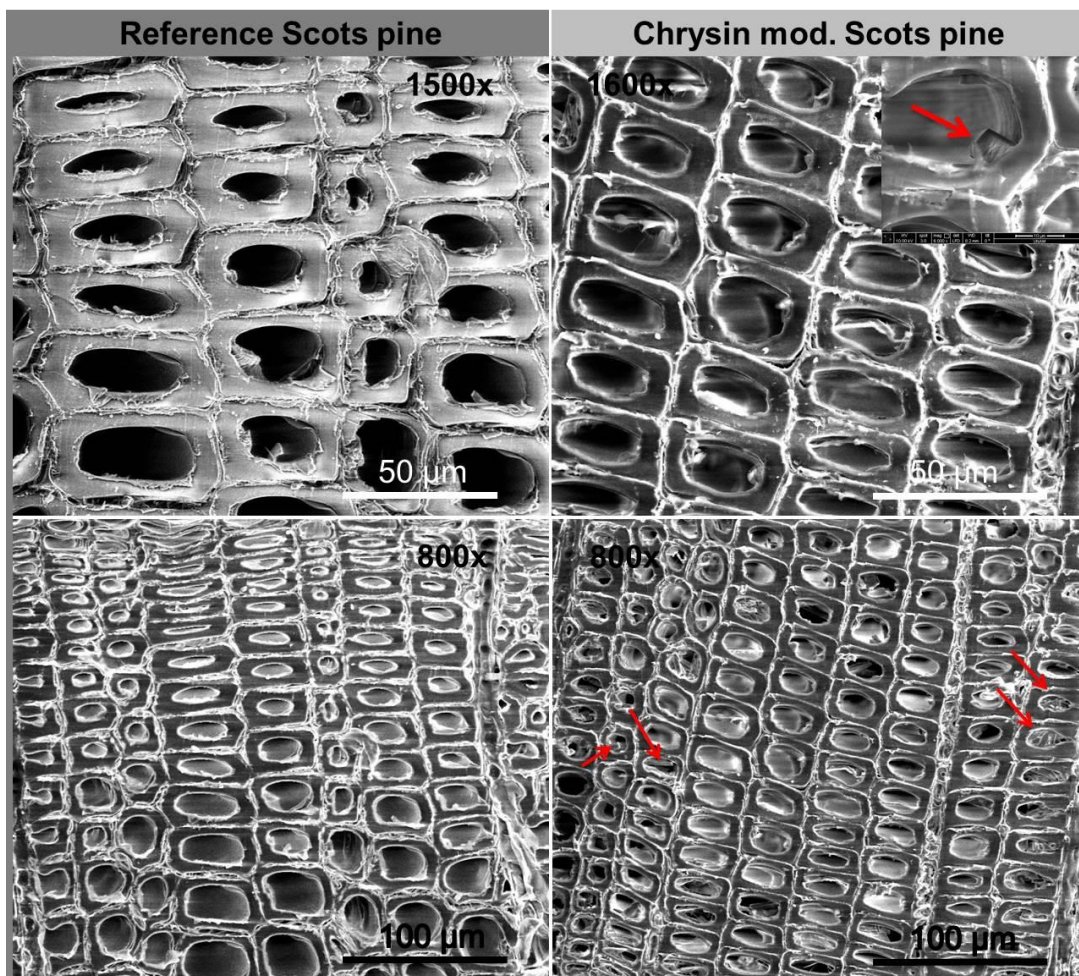
**Fig. 4. a.** FTIR spectra of the reference, pyridine+acetone, tosylated and chrysin modified samples between the wavenumbers 3800 to 800 cm<sup>-1</sup>. **b.** FTIR spectra of reference, pyridine+acetone, tosylated and chrysin modified samples at fingerprint region (1800 to 800 cm<sup>-1</sup>)

### FTIR Analysis

Vibrational spectroscopic techniques (Raman or FTIR) provide valuable information on chemical bonds or interactions that are established between modification reagents and lignocellulosic materials (Gierlinger 2018). Figure 4 contains the FTIR spectra of the reference, pyridine+acetone, tosylated, and chrysin modified samples. From the whole spectra (3800 to 800 cm<sup>-1</sup>) of samples, a general picture of chemical changes due to the modification can be observed (Fig. 4a). In the reference Scots pine, the characteristic bands of wood at the fingerprint region were observed at 1735, 1665, 1602, 1508, 1445, 1423, 1369, 1315, 1261, 1155, 1102, 1051, 1027, and 896 cm<sup>-1</sup> (Traoré *et al.* 2018), as shown in Fig. 4a. In the spectrum of pyridine+acetone, there was no considerable change according to the solvent process. One of the most important outcomes that can be extracted from the spectra in Fig. 4a is reduction of hydroxyl groups (O-H) intensity at wave numbers

of about  $3338\text{ cm}^{-1}$  due to the substitution of hydrophobic tosyl groups in cell wall polymers.

In Fig. 4, the red spectrum belongs to the tosylated wood, and additional bands can be observed at the  $1596$ ,  $1358\text{ cm}^{-1}$ , and  $812\text{ cm}^{-1}$  peaks. The peaks of tosyl groups at  $1596$  and  $1358\text{ cm}^{-1}$  belong to skeletal stretching C-C vibrations and  $812\text{ cm}^{-1}$  belongs to both C-C and  $\text{SO}_2$  stretching vibrations (Parimala and Balachandran 2011). To better understand band differences between the reference and chrysin modified wood, a closer look at the spectra is illustrated in Fig. 4b. To compare chrysin modified wood, a chrysin spectrum is also shown in the figure (orange spectrum). In the FTIR spectrum of chrysin modified wood (dark blue spectrum on the top), some chemical shifts were observed at  $1652/1610/1577$ ,  $1449$ , and  $1356\text{ cm}^{-1}$ . These bands are assigned to C=C stretching of aromatic rings, bending of O-H and C-O-H, and stretching of C-O vibrations, respectively (Ansari 2008). As shown with the blue dashed lines, some of the chrysin bands, which belong to the vibrations (C=C and C-O) of conjugated bonds, had shifted to  $5\text{-}10\text{ cm}^{-1}$  to the higher wavenumber. This kind of band shifts generally indicate intermolecular interactions such as  $\pi\text{-}\pi$ , or a CH- or OH- $\pi$  (Morita *et al.* 2006). In view of the information given, it is thought that most probably aromatic rings and carbonyl group of chrysin were interacting with aromatic groups of lignin or tosyl groups.



**Fig. 5.** Scanning electron microscopy images of reference Scots pine and chrysin modified Scots pine samples under 1500x and 800x magnification



## Morphologic Analysis

SEM images of the reference and chrysin modified wood samples' cross sections are shown in Fig. 5. The structural unity of the cell wall tissue did not incur damage during the reaction of tosylation and further chrysin impregnation. During the modification process, wood samples were immersed completely in pyridine and acetone solvents. For this reason, chrysin molecules were also filled in the lumina. In spite of the presence of residual chrysin after modification process, which the researchers attempted to remove with several portions of water, SEM images indicate that there is still precipitated chrysin crystals filling lumina partially (shown with the red arrow).

## CONCLUSIONS

1. A natural polycyclic and hydrophobic flavonoid was impregnated successfully inside wood cell walls to improve basic wood properties. A pre-treatment was conducted to hydrophobize wood cell walls and to encourage impregnation of the hydrophobic molecule inside cell walls.
2. Dimensional stability and water repellence of Scots pine wood were improved 25% and 33%, respectively.
3. FTIR spectroscopy revealed possible intermolecular interactions between chrysin and the cell wall polymers.
4. SEM images showed that the modification process was a non-destructive method, which provides opportunity to seek further studies.

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