# Dyeing of *Eucalyptus globulus* Veneers with Reactive Dye Using Sequential Vacuum and Varied Pressures

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To investigate the potential application of vacuum-pressure methods for dyeing low-quality hardwood veneers produced from young, small-diameter logs, Eucalyptus globulus veneers were dyed with a 2% solution of the reactive dye Procion Brown PX-2R at a vacuum of -100 kPa for 15 min prior to pressure being applied. The effects of various pressures and pressure times on dye uptake, dye penetration, and colour change were evaluated. Veneers with varying moisture content (MC) were used and were labeled as green veneer (80% ± 5% MC) or dried veneer (12% MC). The dyeing method was based on the results of the preliminary experiments. The vacuum-pressure method had remarkable influence on the dye uptake, dye penetration, and colour change, particularly when the samples were dyed at a pressure of 1000 kPa and pressure time of 120 min. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy results indicated that the reactive dye was able to react with the wood compounds, and scanning electron microscopy (SEM) analysis showed that the ray parenchyma cells provided an effective radial path for dye penetration.

Keywords: Reactive dye; Eucalyptus globulus; Veneer dyeing; Vacuum-pressure method

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#### INTRODUCTION

Because the natural resources of high-quality and large-diameter timber are expensive and limited, a large proportion of the supply requirements for furniture manufacturing, decoration, and wood-based panel processing cannot be fulfilled. Therefore, the global forest industry is making investments in fast-growing plantation timber resources (Deng and Liu 2010; New Forests 2015).

Plantation timbers are young and generally of smaller diameter than the timbers from mature trees. Young timbers have a large amount of sapwood and defects such as encased knots, gum pockets, gum veins, surface roughness, and splits. They are less durable than mature wood and usually have different properties and processing characteristics. Therefore, different processing methods are required.

A majority of *Eucalyptus globulus* plantations established in Australia have been grown to produce pulpwood. This resource is unsuitable for the production of appearance wood products, principally because of the low wood grades, many defects, indistinct grain, and uneven colour. One potential method for enhancing the visual appearance and value of plantation timber is the application of veneer-dyeing technology, which can minimise colour differences within the wood veneer, resulting in a more homogenous colour (Duan and Chang 2002).

Recent studies on wood veneer dyeing have been primarily focused on the dyeing processes of low-density species, such as poplar, basswood, birch, elm, and *Paulownia* (Deng and Liu 2010; Liu *et al.* 2014; Zhang *et al.* 2014; Hu *et al.* 2015; Liu *et al.* 2015), which are characterised by even colour, a small number of defects, and high permeability. Conversely, many plantation eucalyptus have a medium to high density, many defects, uneven colour, and low permeability. Therefore, a detailed study is required to investigate the dyeing process for eucalyptus veneers.

Because several common dyes, such as acid and mordant dyes, have been banned or restricted because of environmental issues, reactive dyes have been highly valued by the wood-dyeing industry (Deng and Liu 2010). An investigation by Rattee (1962) indicated that reactive dyes have a potential application for dyeing methods that offered comparable costs because of the simplicity of the operation and the reduced dye consumption as a result of the high rate of fixation. Moreover, reactive dyestuff has bright color characteristics, good washing fastness, and complete chromatography. For that reason, reactive dyes have good colour fastness to wet treatments, as well as a broad colour range, and have gradually replaced direct dyes, vat dyes, and sulphur dyes in the colouration of cellulose-based materials such as cotton and viscose (Zhang and Yang 2008).

Many wood veneer dyeing methods have been applied, such as soaking dyeing, vacuum dyeing, and vacuum-pressure dyeing, which combines vacuum and pressure dyeing. However, the results have shown many disadvantages. For example, dyed veneers were not entirely penetrated, or they were easily damaged during the dyeing process or curved after dyeing and drying (Chang *et al.* 2009).

The aim of this study was to investigate the feasibility of using sequential application of vacuum followed by pressure of different levels and durations for dyeing *Eucalyptus globulus* veneers with a reactive dye at ambient temperature ( $20 \text{ °C} \pm 3 \text{ °C}$ ). The effect of various pressures and pressure times on dye uptake, dye penetration, and colour change were investigated. In addition, attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy and scanning electron microscopy (SEM) were used to explore the mechanism of interaction between dye molecules and wood fibers.

#### EXPERIMENTAL

#### Material Preparation, Colour Application, and Equipment

#### Sample preparation

Peeled veneers from a commercial plantation-grown *Eucalyptus globulus* in Victoria, Australia were selected to conduct dyeing experiments. The plantation was established in June 2000 by Australian Bluegum Plantations Company, and the trees were harvested in December 2015. Veneer samples (L: 100 mm × T: 50 mm × R: 2.6 mm) were prepared from sapwood and heartwood at the green moisture content (MC) of 80%  $\pm$  5% and dry moisture content of 12%.

#### Dye selection

The reactive dye Procion Brown PX-2R, at a concentration of 2%, was selected for the vacuum-pressure method. The dye was purchased from Dyechem Australia Pty Limited (Melbourne, Australia). Procion Brown PX-2R is a monochlorotriazine reactive dye that

reacts with the hydroxyl (OH) groups in cellulose under alkaline conditions. Because this dye has slightly lower reactivity compared to dichlorotriazine dyes, the dye should penetrate more uniformly into the gross structure of the veneer. Furthermore, based on the results of preliminary tests conducted using various dyes, the reactive dye resulted in a significantly higher dye penetration than the other dyes, such as direct dyes (Nguyen *et al.* 2018a,b).

#### **Dyeing Method**

#### Dye solution preparation

A 2% solution of Procion Brown PX-2R was prepared by dissolving 2 g in 100 mL of water using a standard flask. All dye solutions were prepared at ambient temperature  $(20 \text{ }^{\circ}\text{C} \pm 3 \text{ }^{\circ}\text{C})$  in the laboratory.

#### Vacuum pressure method

A vacuum pressure method was selected for the veneer-dyeing study based on the results of preliminary tests conducted using soaking and vacuum-pressure methods (Nguyen *et al.* 2018a,b). A dye penetration of 100% was achieved when using the vacuum-pressure method.

The wood treatment plant at the Creswick campus, University of Melbourne was used for the dyeing trials. The plant consists of the following parts: (1) compressor – generates compressed air that is used to achieve desired pressure during impregnation treatment; (2) cylinder for air storage (prompt air) – the compressed air generated by the compressor is stored in the cylinder and subsequently used during pressure impregnation of the preservative; (3) vacuum pump – creates a vacuum in the treatment vessel to remove the air and the excess preservative from the wood during the initial and final stages of preservative treatment, respectively; (4) treatment vessel – samples are submerged in treating solution and kept in the treatment vessel for pressure impregnation. In the treatment plant, high pressures (up to 1500 kPa = 1.5 MPa) can be applied. A single dyeing schedule was used for the wood veneer dyeing process (Fig. 1).



Fig. 1. Scheme of the dyeing process

The schedule was as follows: initial vacuum of -100 kPa applied for 15 min; required pressure level applied (kPa) for required time (min). The dyeing time was referred to as the pressure time.

#### Experimental framework

The following experimental framework was used for the veneer-dyeing study, with the following conditions (Table 1). Procion Brown PX-2R (2% dye solution) was used, with 20 g/L of sodium chloride mixed with the dye. All experiments were conducted at ambient temperature ( $20 \,^{\circ}C \pm 3 \,^{\circ}C$ ). A vacuum of -100 kPa was applied for 15 min prior to pressure application. The selection of the constant conditions and the veneer dyeing variables was based on the preliminary trials conducted at RMIT University and the University of Melbourne (Nguyen *et al.* 2018a,b).

According to the experimental framework developed for the study, the total number of veneer samples was 432 (*i.e.*, 12 specimens  $\times$  36 dyeing variable combinations).

Dyeing Variables		Combinations of Variables Implemented during Experiments										
Moisture Content (%)	Green Veneers (80% ± 5% MC)				Dry Veneers (12% MC)							
Samples	0,	Sapwo	od	d Heartwood		Sapwood		Heartwood				
Pressure Time (min)	60	90	120	60	90	120	60	90	120	60	90	120
Pressure Level (kPa)	500	750	1000	500	750	1000	500	750	1000	500	750	1000

**Table 1.** Experimental Framework used for Veneer-Dyeing Study

#### Measurement of the Dye Uptake

The percentage uptake of liquid was used to measure absorption (Eq. 1). It was assumed that weight only changed during liquid soaking because of the absorption of liquid into the void volume of the wood. The maximum possible absorption of each specimen was calculated as a percentage of void volume filled (saturation) (Sugiyanto 2003),

$$S, \% = 100 x \frac{U_1}{F_r}$$
 (1)

where *S* is the percentage saturation or percentage of uptake (%),  $U_1$  is the initial liquid uptake (kg/m<sup>3</sup>), and  $F_r$  is the maximum possible absorption of liquid (kg/m<sup>3</sup>) (Eq. 2),

$$F_{\rm r} = F \times D_{\rm r} \tag{2}$$

where *F* is the maximum possible absorption of water  $(L/m^3)$  (Eq. 3) and  $D_r$  is the density of the liquid (kg/L),

$$F = 1000 - (D_{\rm w} \times (\rm{MC} + 66.7) / 100)$$
(3)

where  $D_w$  is the basic density of wood (kg/m<sup>3</sup>) and MC is moisture content (%).

#### Measurement of the Dye Penetration

It is very difficult to measure the cross-section of a veneer using a caliper, because the veneer is thin and, in most cases, it contains irregular areas in which the penetrated dyes cannot be found. Therefore, ImageJ (NIH, Bethesda, MD) was used to compute the areas. A dyed veneer was cut using a sharp knife. Then, a 5MP-USB microscope was used to take pictures of the cross-section of the dyed veneer. The ImageJ software was then used to compute the area and the percentage of dye penetration. This program has been shown to be the most suitable method for analysis and visualization of 2D and 3D data (Gurau *et al.* 2013)

#### **Measurement of Colour Differences**

The colour measurements were recorded using a BYK-Gardner digital colour apparatus (Geretsried, Germany) at ambient temperature (20 °C  $\pm$  3 °C), and the results were presented in the CIELAB colour system. The *L*\*, *a*\*, and *b*\* colour coordinates were calculated based on the illuminant D65 (representing Northern daylight at noon and the international standard for daylight exposure) and an observation angle of 10° (Hunter and Harold 1987).

Colour measurements were performed on the tight sides of all veneer samples (green and dry) prior to the dyeing process. After the dyeing process, the green dyed veneers were measured to compare the previous measurements on untreated green veneers, while dry dyed veneers were measured once they were dried to 12% moisture content.

The colour of every sample was scanned at four locations, and the result was automatically calculated by the BYK-Gardner digital colour apparatus as the average value of the four scans. The same locations were used for measuring the colour of the veneer before and after dyeing. The locations for the colour measurements in each test sample were carefully chosen to avoid knots and other defects.

According to the colour coordinates  $L^*$ ,  $a^*$ , and  $b^*$ , the change in colours and their locations were determined. The  $L^*$  axis specifies the lightness and runs vertically in the range from black (0) to white (100). The coordinate  $a^*$  represents green at negative ( $-a^*$ ) values, and red at positive ( $+a^*$ ) values. The  $b^*$  axis is the blue-yellow square, where negative ( $-b^*$ ) values are blue, and positive ( $+b^*$ ) values are yellow. Both  $a^*$  and  $b^*$  are positive/negative coordinates defining the hue and intensity of the colour.

The total change of colour,  $\Delta E^*$ , is commonly used to represent a colour difference,

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{4}$$

where  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  are the changes between the sample values before and after dyeing of  $L^*$ ,  $a^*$ , and  $b^*$ , respectively.

To determine the actual change in colour, the individual colorimetric components  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$ , or  $\Delta L^*$ ,  $\Delta C^*$ , and  $\Delta H^*$  need to be used. The calculation and interpretation of the changes were performed as follows (Fig. 2). A low  $\Delta E_{L^*a^*b^*}$  corresponds to a low colour change or a stable colour. According to Lovrić *et al.* (2014), the colour differences of treated veneers can be classified by  $\Delta E$  as given in Table 2. This classification was applied for the assessment of colour changes of the dyed veneers.



Fig. 2. Calculation and interpretation of the colour differences

No.	Colour Change (ΔE)	Description
1	Δ <i>E</i> < 0.2	No noticeable difference
2	2 $0.2 \le \Delta E < 2$ Small difference	
3	$2 \le \Delta E < 3$	Colour differences noticeable at high quality screen
4	4 $3 \le \Delta E < 6$ Colour differences noticeable at middle quality set	
5	$5  ext{ } 6 \leq \Delta E < 12  ext{ } Great difference  ext{}$	
6	Δ <i>E</i> ≥ 12	Different colours

**Table 2.** Classification of the Color Difference by  $\Delta E$ 

#### Scanning Electron Microscope (SEM) Analysis

Scanning electron microscopy was used to investigate changes in the wood structure of the dyed and undyed veneers. The SEM micrographs of the samples revealed in detail the mechanisms of wood veneer dyeing. The distribution of the reactive dye within the wood cell cavity and wood ray was observed using a SEM (FEI Teneo VolumeScope, ThermoFisher Scientific, Waltham, MA, USA) at an accelerating voltage of 10 kV.

#### **ATR-FTIR Spectroscopy**

Attenuated total reflectance - Fourier transform infrared (ATR-FTIR) spectroscopy was used to characterise the surface chemical composition of the dyed veneers. The spectra were obtained using attenuated total reflectance (ATR) and collected using a single reflection diamond accessory. The ATR crystal was cleaned with methanol, then air-dried. The background was collected with the crystal exposed to the air. All samples were placed onto the crystal surface of the FTIR spectrometer (Bruker ALPHA FTIR Spectrometer, Billerica, MA, USA). The spectra were collected in transmittance mode by a total of 32 scans in the range of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> at a resolution of 2 cm<sup>-1</sup>. OPUS software (Bruker, Billerica, MA, USA) was used to select the peaks of the transmittance bands. The veneer samples that were dyed at a pressure of 1000 kPa for 120 min were used in the SEM analysis and ATR-FTIR spectroscopy because these variables provided the highest dye uptake and penetration.

#### **Statistical Analysis**

An analysis of variance was conducted on the dye uptake, dye penetration, and colour differences with various factors of the dyeing process as explanatory variables. Main effects and two-factor interactions were included in the model. The assumption of constant variance was checked with a plot of residual values *vs*. fitted values. Main effects were considered to be significant if P < 0.05, and two-factor interactions were reported for approximately P < 0.01 or. Least significant difference (LSD) values at P = 0.05 were used to estimate the variability between the means of the samples for each combination of factors. The software GENSTAT (16th Edition, VSN International Ltd, Hemel Hempstead, UK) was used for statistical evaluation of the data.

### **RESULTS AND DISCUSSION**

#### Effect of Pressure Level and Time on Dye Uptake

The effects of various pressure levels and times on dye uptake are presented in Fig. 3. The analysis of variance showed a highly significant effect of all factors: moisture content, sample type, pressure time, and pressure level (P < 0.001). None of the interactions were significant. The factors' means are shown in Table 3 with the LSDs.

There were highly significant differences between green and dry samples and sapwood and heartwood samples in relation to dye uptake (P < 0.001). The dye uptake of the dry samples was higher than that of the green samples for all pressure levels and times. This can be explained based on the idea that the amount of the dye that can be contained in the dyed wood depends on the available amount of void space in the wood cell cavities. Since the internal wood empty spaces, which are in the cell wall, have been filled with water at a high moisture content (85%), this limits the dye uptake into the wood, while at the low moisture content (12%), more dye can penetrate into the wood due to existence of more empty spaces.

Furthermore, with increasing the wood moisture content, swelling occurs in the cell-wall and therefore, the volume of cell-wall pores or empty spaces decreases, which results in reducing the dye uptake into the wood.

Factor	Level	Mean	Least Significant Difference (LSD)
	Green veneer (80% ± 5%)	6.4	
MC (%)	Dry veneer (12%)	10.1	0.27
Sampla Type	Heartwood	7.8	0.27
Sample Type	Sapwood	8.7	0.27
	60	7.9	
Pressure Time (min)	90	8.1	0.34
	120	8.7	
	500	7.7	
Pressure Level (kPa)	750	8.2	0.34
	1000	8.9	]

Table 3. The Influence of the Main Effects on Dye Uptake

**Green Sapwood Veneer** 







Fig. 3. Effect of various pressure times and levels on dye uptake. Data are reported as the mean dye uptake of the samples

Dye uptake of the dry sapwood samples reached its peak of 11.5% at a pressure of 1000 kPa for 120 min, while the peak of 11.3% for the dry heartwood samples occurred at a pressure of 1000 kPa for 90 min. It could be argued that using liquid uptake-based method of measuring the percentage of dye uptake may lead to different quality assessments compared to a spectrophotometric method for dye bath absorption determination (Nguyen *et al.* 2018b).

The use of a liquid uptake-based method that is based on the wood veneer weight change before and after dyeing process may not determine the exact obtained absorption because it reflects surface saturation which is influenced by the veneer surface roughness, lathe checks. Therefore, the samples dyed at a pressure of 1000 kPa for 90 min may resulted in an inaccurate value of dye uptake, which could lead to an incorrect assessment of the performance of veneer dyeing process. For this reason, in addition to the dye uptake, the determination of the dye penetration into dyed veneer was carried out to confirm the effect of the dyeing parameters on dye uptake. This may provide an indication as to whether dye uptake can be used as an adequate criterion for selecting optimal dyeing parameters for the wood veneer dyeing process.

#### Effect of Pressure Level and Time on Dye Penetration

Figure 4 demonstrates the effect of pressure levels and times on dye penetration. The main effects of sample type (sapwood/heartwood), pressure time, and pressure level were highly significant (P < 0.001), while the main effect of moisture content and interactions between the factors were not significant. The factor means are shown in Table 4, together with the LSDs.

The dyeing parameters that resulted in the highest dye penetration were the same for both green and dry veneers. There was no significant difference (P = 1.00) between the green and dry veneers in terms of dye penetration. Dye penetration increased with increasing pressure level and time for both green and dry dyed veneer samples. The application of the pressure level of 1000 kPa and the time of 120 min had noticeable effects on dye penetration (P < 0.001). Both the sapwood and heartwood of green and dry samples obtained 100% dye penetration.

Factor	Level	Mean	Least Significant Difference (LSD)
Sampla	Heartwood	89.9	0.62
Sample	Sapwood	92.4	0.03
	60	85.7	
Pressure Time (min)	90	91.4	0.77
	120	96.4	0.77
	500	87.6	
Pressure Level (kPa)	750	90.3	0.77
	1000	95.6	

Table 4.	The Influence	of Main Effects	s on Dye Penetration
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Green Sapwood Veneer





Dry Sapwood Veneer







Fig. 4. Effect of various pressure times and levels on dye penetration. Data reported as the mean dye penetration of the samples

Dye penetration and dye uptake are the most important parameters for the dyeing process because they affect the quality of the dyed veneers. It could be argued that the measurements of the percentage of dye penetration and dye uptake may lead to different quality assessments. For instance, the dye uptake measurement, which is based on the veneer weight change before and after the dyeing process, may not determine the exact absorption of the dye because the results could be affected by the veneer surface saturation, which is influenced by the veneer surface roughness and lathe checks. This effect may result in an inaccurate value for the dye uptake, which could lead to an incorrect assessment of the performance of the veneer-dyeing process. However, the results indicated a similar trend in the correlation between the dye uptake/dye penetration and the dyeing parameters.

#### Effect of Pressure Level and Time on Colour Change

The results of the effect of the pressure levels and times on the colour change are presented in Fig. 5. The main effects of moisture content and pressure time were highly significant (P < 0.001), while the main effect of pressure level was significant (P = 0.006). The factor means are shown in Table 5 with the LSDs. The moisture content by sample type interaction was also highly significant (P < 0.001). The means of the factor combinations and the associated LSD are shown in Table 6.

Factor	Level	ΔE <sub>mean</sub>	Least Significant Difference (LSD)	
MC (%)	Green veneer (80% ± 5%)	15.3	0.26	
MC (%)	Dry veneer (12%)	29.2	0.30	
	60	21.3		
Pressure Time (min)	90	22.1	0.45	
	120	23.4		
	500	21.8		
Pressure Level (kPa)	essure Level (kPa) 750		0.45	
	1000	22.6		

Table 5	The Influence	of Main	Effects o	n Colour	Differences
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Table 6. The Influence of Moisture Content	by Sample Interaction on Colour	Change
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Maistura Contant (%)	Sample	۸E	
Moisture Content (%)	Heartwood	Sapwood	Δ⊏mean
Green veneer (80% ± 5%)	15.6	14.7	15.3
Dry veneer (12%)	28.3	30.1	29.2
Mean	22.0	22.4	22.2
LSD		0.52	

In general, the pressure level and time that achieved the greatest colour change (P < 0.01) in both green and dry veneer samples were 1000 kPa and 120 min, respectively. The colour change in the dry sapwood and heartwood samples was approximately double that in the green sapwood and heartwood samples (P = 0.001). Based on the colour difference classification shown in Table 2, the colour change ( $\Delta E$ ) of all dyed veneer samples exceeded 12. Therefore, according to the classification of the colour difference by  $\Delta E$ , there were different colours between the dyed and undyed wood veneer samples. Interestingly, there was a similar colour change (P > 0.1) in both green sapwood and heartwood samples and dry sapwood and heartwood samples with increasing pressure times and levels.







Pressure levels, kPa



**Dry Heartwood Veneer** 



The colour change of the dyed green sapwood veneers reached its greatest value of 16.69 at a pressure of 1000 kPa for 120 min. There were similar results (16.31, 16.33, and 16.47) in the colour change of the green heartwood samples at the pressure levels of 500, 750, and 1000 kPa, respectively, for 120 min.

There was a highly significant increase (P = 0.001) in the colour change in the dry dyed samples compared to the green samples. The highest colour change was also obtained in the dry sapwood samples at a pressure of 1000 kPa and pressure time of 120 min. However, the colour change in the dry sapwood samples was 32.15, which was double that of the green sapwood samples (16.69). Furthermore, there was little difference (P = 0.134) between the colour change in the dry sapwood and heartwood samples at the various pressure levels and times.

Figure 6 is an example of the colour difference between the undyed and dyed wood veneer with the optimum dyeing parameters.



Fig. 6. Photos of undyed and dyed wood veneer

#### **SEM Analysis**

The SEM micrographs of undyed and dyed wood veneers in radial, tangential, and cross sections are shown in Fig. 7.



Fig. 7. SEM micrographs of undyed and dyed wood veneer in radial, tangential, and cross sections

The fundamental cell structure of hardwood species consists of three cell formations: vessels, fibers, and parenchyma cells (axial and ray), which are produced inside of the cambium layer. Liquid enters the wood primarily through the vessels, and then penetrates the vasicentric tracheid, vertical parenchyma, and finally the fibers, through the pit pairs (Wardrop and Davies 1961).

In this study, the flow of the dye was restricted to the transverse direction. Bulk flow of the dye was observed from the rays to the vessels through pit pairs. However, as can be seen from the radial and cross sections of the undyed wood veneers in Fig. 7 (R1 and C1), various pits were occluded with inclusions. Therefore, the dye penetration of the veneer is very poor if the normal soaking method is used for the dyeing process (Nguyen *et al.* 2018a). When the samples were subjected to a high level of pressure, the dye was able to reach fiber lumens from vessels and parenchyma cells through pit pairs. Almost all of the fibers of the dyed wood veneers were filled, indicating flow from the vessels through the pits (Fig. 7, R2 and C2)

Ray parenchyma cells are typically impermeable. However, in some cases, they can be the primary path for penetration of fluids (Siau 1984). The SEM image R2 in Fig. 7 shows that the ray parenchyma cells provided an effective radial path for dye penetration. This path resulted in the ray parenchyma of the dyed wood veneers being filled with a large amount of the dye molecules compared to the undyed veneer samples (Fig. 7, R1).

#### Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR)

The ATR-FTIR spectra of the undyed (blue) and dyed (red) wood veneer in the range of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> are shown in Fig. 8. The peak of the hydroxyl stretching bands was at 3392 cm<sup>-1</sup>, which indicates that a large amount of cellulose and hemicellulose was present in the *Eucalyptus globulus* veneer. The peak at 2963 cm<sup>-1</sup>, attributed to the C-H stretching bands, represents the presence of cellulose, hemicellulose, and lignin.



Fig. 8. ATR-FTIR spectra of undyed (blue) and dyed (red) wood veneer in the range of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>

The cell walls of wood primarily consist of cellulose, hemicellulose, and lignin. Generally, O-H and C-H stretching bands have contributions from all three chemical components (Shi *et al.* 2012). Therefore, the fingerprint region in the range of  $1800 \text{ cm}^{-1}$  to  $800 \text{ cm}^{-1}$  (Fig. 9) was selected to analyse the chemical functional groups present on the wood veneer surface because this range

is the most sensitive to chemical changes (Pucetaite 2012). The band assignments of the peaks in the range of the fingerprint region are summarized in Table 7. The assignments of the bands are approximate because the chemistry of wood is complex, and many different vibrations have input on the band positions and intensities.

The ATR-FTIR spectra (Fig. 9) and band assignments (Table 7) demonstrate that there was reaction between the wood and the dye.



**Fig. 9.** ATR-FTIR spectra of undyed (blue) and dyed (red) wood veneer in the range of 1800 cm<sup>-1</sup> to 800 cm<sup>-1</sup>

Wavenumber (cm <sup>-1</sup> )	Chemical Structure Assignments
1736	C=O stretch in functional groups in hemicelluloses
1650	C=O stretching vibration of conjugated carbonyl of lignin
1592	C=C stretching of the aromatic ring in lignin
1489	C-C stretch, CH and OH wag in cellulose and hemicellulose, CH
	deformation in lignin
1456	-CH <sub>3</sub> and -CH <sub>2</sub> unsymmetrical bending in lignin
1424	CH and OH wag in cellulose and hemicellulose, CH deformation in
	lignin
1370	Bending vibration of C-H in cellulose and hemicellulose
1309	C-O stretch in syringyl ring in lignin, CH and OH wag in cellulose and
	hemicellulose
1225	C-O stretch in syringyl ring in lignin, CH and OH wag in cellulose and
	hemicellulose
1163	C-O-C bridge vibration, asymmetric C-O stretch in cellulose and
	hemicellulose
1108	C-O and C-C stretch in cellulose and hemicellulose
1033	C-O stretching vibration (cellulose, hemicellulose and lignin)
976	C-O stretch in a ring in cellulose and hemicellulose
898	C-H deformation in amorphous cellulose

Table 7. Characteristic Band	Assignments of ATR-FTIR S	pectra for Dyed Wood Veneer
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**Sources:** Pandey and Pitman 2003; Vu and Jian 2010; Pucetaite 2012; Shi *et al.* 2012; Hu *et al.* 2015; Liu *et al.* 2015; Malik *et al.* 2018

The chemical structure of lignin for a large number of the functional groups of the dyed wood veneer (1650 cm<sup>-1</sup>, 1592 cm<sup>-1</sup>, 1489 cm<sup>-1</sup>, 1456 cm<sup>-1</sup>, and 1424 cm<sup>-1</sup>) indicated degradation via phenoxy radical reactions. Moreover, it was apparent that the chemical structures of cellulose and hemicellulose of the dyed wood veneer (1489 cm<sup>-1</sup>, 1424 cm<sup>-1</sup>, 1370 cm<sup>-1</sup>, 1309 cm<sup>-1</sup>, 1225 cm<sup>-1</sup>, 1163 cm<sup>-1</sup>, 1108 cm<sup>-1</sup>, 1033 cm<sup>-1</sup>, 976 cm<sup>-1</sup>, and 898 cm<sup>-1</sup>) were degraded after the dyeing process.

## CONCLUSIONS

- 1. The vacuum-pressure method, with application of vacuum followed by pressure for veneer dyeing, resulted in full dye penetration (100%) in both green and dry heartwood samples at a pressure of 1000 kPa and a vacuum of -100 kPa for 15 min with the reactive dye Procion Brown PX-2R, at a concentration of 2%.
- 2. The greatest colour change in both green and dry veneer samples was achieved at a pressure level of 1000 kPa and a pressure time of 120 min. However, the colour change in the dry samples was approximately double that of the green samples.
- 3. The ATR-FTIR analysis indicated that the dye was able to react with cellulose, hemicellulose, and lignin. The SEM analysis showed that the ray parenchyma cells provided an effective radial path for dye penetration. This path resulted in the ray parenchyma of the dyed wood veneers being filled with a large amount of the dye molecules compared to the undyed veneer sample.
- 4. Based on the results of the colour differences of the dyed green and dry wood veneer, it is suggested that manufacturers in the furniture and interior design sector should consider the selection of dry or green veneers for the dyeing process in order to meet the consumers' desire.

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