Enhancing the Properties of Low Density Hardwood *Dyera costulata* Through Impregnation with Phenolic Resin Admixed with Formaldehyde Scavenger


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**Abstract**: The formaldehyde emission, properties and decay durability of *Dyera costulata* wood, impregnated with low molecular weight phenol formaldehyde (LmwPF) resin mixed with urea were investigated. The air-dry wood was impregnated with 20-40% LmwPF (M₆, 600) mixed separately with urea (30% based on solid PF), partially cured at 60°C for 30 min and subsequently heated at 150°C for 60-120 min. The treatments had successfully reduced the formaldehyde emission (FE) of the impreg and the degrees of reduction depend on curing time. Statistical analyses showed that the concentration of resin affected the density, stiffness, water absorption and thickness swelling, while the curing time affected the density, polymer loading, water absorption and thickness swelling. Impregnated product had higher MOR, MOE and dimensional stability compared to the untreated wood. The treatments rendered the impregnated product with approximately 20% in anti-swelling efficiency and had also changed the wood into highly resistant to fungal decay.

**Key words**: Impreg, phenol formaldehyde, urea, scavenger

**INTRODUCTION**

Chemical treatment of wood has been intensively investigated to improve the properties of low density wood and make them more usable in assessing the shortfall of wood supply. Numerous treatment systems have been proposed to improve wood properties, particularly for wood used under conditions where it is exposed to moisture or biological attack.

Impregnation with Phenol Formaldehyde (PF) resin followed by curing under heat has been known to provide tremendous enhancement in properties, which include mechanical strength, dimensional stability (Hill, 2006) and durability against decay and termite attack (Ryu et al., 1991; Aikifei, 2010). This product is known as impreg (Rowell, 2005). Kajita and Imamura (1991) used low molecular weight formaldehyde resin (LmwPF) to improve the physical and biological properties of particle boards while, Anwar et al. (2006) and Loh et al. (2011), respectively, used this resin to enhance the properties of laminated bamboo and oil-palm stem veneer. The LmwPF resin managed to swell the cell wall without bonding to it. The PF resin with a molecular weight (MW) of 290-480 was able to penetrate the cell wall and increased stability (Rowell, 2005) but the PF resin with MW of 820 just remained in the cell lumen without gaining much stability (Furuno et al., 2004). Impregnation of low density wood with PF followed by compressing at high temperature has also been proven in enhancing the bending strength, dimensional stability and durability against fungal attack (Zaidon et al., 2010). This product, known as compreg, normally has Modulus of Rupture (MOR), Modulus of Elasticity (MOE) and hardness greater than the untreated wood due to the increase in density.

However, besides the positive effects of this treatment, the treated product releases free formaldehyde. It is generated from free, unreacted formaldehyde during the process of curing. When exposed to high temperature and humidity during polymerization, some of the methylene groups in the oligomeric chains of the LmwPF resin will release undesirable free formaldehyde into the surrounding (Hoong et al., 2010). One way to capture this free formaldehyde is by using the formaldehyde catcher/scavenger (Roffael, 1993). There are many formaldehyde scavengers that have been introduced into the treatment system which include urea, ammonium
phosphate, potassium sulphite and sodium thiosulphate. However, urea is preferable due to its low cost and has been proven able to reduce the formaldehyde emissions from the compreg products made from low density wood, sesenduk (Endospernum diadenum) and mahang (Macaranga spp.) (Zaidon, 2009). It is expected that the introduced urea will react with the free formaldehyde and form a rigid cross-linked polymer of urea formaldehyde.

In this study, urea was mixed with the LnwPF solution before it was used in the impregnation of low density wood. This study reports the formaldehyde emission, properties and durability of the impreg made from the low density hardwood jelutong (Dyera costulata). The effect of PF concentration and curing time on the properties of the treated wood were also evaluated.

**MATERIALS AND METHODS**

**Materials:** The jelutong wood used in this study was obtained from Ayer Hitam Forest Reserve, Puchong, Selangor. The treating solution was composed of low molecular weight phenol formaldehyde (LnwPF) resin (M₉₆00, 45% solid) purchased from Malaysian Adhesive Chemical, Shah Alam. Urea granules were used as the formaldehyde scavenger which was mixed with the PF resin.

**Samples preparation:** PF resin was diluted with distilled water to 20%, 30% and 40% concentrations. Urea was mixed separately into the three solutions. In the earlier work, it was found that the urea concentration in the range of 10-30% (based on solid PF) was able to reduce FE from the impreg and compreg made from the low density wood, Endospernum diadenum and the FE reduction increased with the urea concentration (Zaidon, 2009). In this case, 30% of urea (based on solid PF) as the formaldehyde scavenger was used. The pre-conditioned wood (MC = 12%) which was free from defects, was flat sawn into the samples (the width is the tangential surface) with a nominal dimension of 150 mm long, 50 mm wide and 5 mm thick. The untreated samples served as the control for comparison purposes.

**Impregnation treatment process:** The pre-weighed samples were vacuum-pressure impregnated with the solution separately in an impregnation apparatus. The treating cycle consisted of a 15 min initial vacuum of 85 kPa followed by filling the set-up with the treating solution under vacuum. A final pressure of 340 kPa was applied for 30 min at an ambient temperature. The impregnated samples were immediately weighed before being partially cured at 60°C for 30 min and subsequently cured at 150°C for 60, 90 and 120 min. In a preliminary work, Zaidon (2009) found that a minimum of 60 min was required to cure the PF resin in the wood of the same thickness. All the treated samples were then conditioned at 65±2% RH and 25±2°C until a constant weight was obtained. The density and Weight Percent Gain (WPG) for each impreg were then determined using the following equations:

\[
\text{Density (kg m}^{-3}\text{)} = \frac{W_f}{V_f} \tag{1}
\]

\[
\text{WPG} (\%) = 100 \left[ \frac{W_f - W_i}{W_i} \right] \tag{2}
\]

where, \( W_f \) is the weight of the sample after curing and conditioning, kg, \( V_f \) is the volume of the sample after curing and conditioning m³ and \( W_i \) is the initial weight of the sample, kg.

**Formaldehyde emission (FE) test:** The impreg samples with or without admixed urea were subjected to the FE test after conditioned to a constant weight. The test was carried out following the method specified in the Malaysian Standard (MS, 2005) Wood-based panels-Determination of Formaldehyde Emission by the Dessoricator Method. Calibration curve was first produced from a standard formaldehyde solution by iodometric titration. About 8-10 test pieces (total surface area of 1800 cm²) were placed in a desiccator above a plastic container filled with 300 mL of distilled water. They were left in the laboratory for 24 h at an ambient temperature. The background formaldehyde was prepared using a desiccator without the test piece. The formaldehyde absorbance was measured photometrically at 412 nm wavelength and these values were used to determine the FE using Eq. 3, as follows:

\[
G = f \times (A_d - A_b) \times 1800/S \tag{3}
\]

where, \( G \) is the concentration of formaldehyde due to the test pieces, ppm, \( A_d \) is the absorbance of the solution from the desiccators containing the test pieces, \( A_b \) is the absorbance of the background formaldehyde solution, \( f \) is the slope of the calibration curve for the standard formaldehyde solution, ppm and \( S \) is the surface area of the test pieces, cm².

**FT-IR spectroscopy analysis:** The infrared spectum analysis was performed on the impreg samples using a PerkinElmer Spectrum 100 Series FT-IR, equipped with a CsI detector attached to the ATR unit. The FTIR-UATR spectra were recorded in the wave number ranging from 4000-400 cm⁻¹.
Evaluation of dimensional stability: The degree of dimensional stability was determined by estimating and comparing the anti-swelling efficiency (ASE), Water Absorption (WA) and Thickness Swelling (TS) of the treated and control samples of 20×20 mm dimensions. The swelling process was done through 15min vacuum followed by soaking in distilled water for 24 h (Ashaari et al., 1990a). The weights before and after swelling process were measured. The volumetric swelling coefficients (S), anti-swelling efficiency (ASE), water absorption (WA) and thickness swelling (TS) were calculated using the following equations:

\[ S(\%) = 100 \left( \frac{V_t - V_i}{V_i} \right) \]  
\[ \text{ASE}(\%) = 100 \left( \frac{S_t - S_i}{S_i} \right) \]  
\[ \text{WA}(\%) = 100 \left( \frac{W_t - W_i}{W_i} \right) \]  
\[ \text{TS}(\%) = 100 \left( \frac{T_t - T_i}{T_i} \right) \]

where, \( V_i \) is the volume of the sample after soaking, mm\(^3\), \( V_t \) is the volume of oven-dried sample, mm\(^3\), \( S \) is the untreated volumetric swelling coefficient, mm\(^3\), \( S_t \) is the treated volumetric swelling coefficient, mm\(^3\), \( W_i \) is the weight of sample after soaking, g, \( W_t \) is oven-dried weight of the sample before soaking, g, \( T_t \) is the thickness of the sample after soaking, mm and \( T_i \) is the oven-dried thickness of the sample before soaking, mm.

The treated pieces were also exposed to water vapour at 95% humidity until equilibrium. Graphs of WA and TS versus days of exposure were plotted. In this study, the exposure time in water vapour was taken to be completed when the untreated samples achieved the constant weight. This took approximately 24 days.

Evaluation of mechanical properties: Static bending test was performed according to the British Standard BS 373:1957 (BSI, 1957) with a modification of specimen size (20 by 150 mm) to compare the strength and stiffness of the treated and untreated samples. The specimens were placed on a 50 kN Instron universal testing machine, on a fixed support with a span of 120 mm and were tested under a static load with a crosshead speed of 6.4 mm min\(^{-1}\). The mechanical properties calculated from the load deflection curves included modulus of rupture (MOR) and modulus of elasticity (MOE).

Decay resistance test: Decay resistance was tested according to the American Standard Test Method (ASTM D 1413-99) for Wood Preservatives by Laboratory Soil-Block Cultures (ASTM, 1999). The specimens (20×20×5 mm) were first conditioned at 25±2°C and 65±2% RH until a constant weight was reached. The pre-weighed treated and untreated specimens were exposed to the white rot fungus (Pycnoporus sanguineus) for 12 weeks. After exposure to the fungus, the specimens were again conditioned until they reached a constant weight. The weight loss due to the decay was calculated using Eq. 8, as follows:

\[ WL(\%) = 100 \left( \frac{W_t - W_c}{W_t} \right) \]

where, \( W_t \) is the weight of conditioned specimen before test, g and \( W_c \) is the weight of conditioned specimen after test, g.

Statistical analysis: Statistical analysis was carried out using a two-way analysis of variance (ANOVA) to analyze any changes in the property values among the treatment combinations. The mean was separated using the Duncan Multiple Range Test (DMRT) at p≤0.05.

RESULTS AND DISCUSSION

Formaldehyde emission of the Impreg: The calibration curve produced from iodometric titration is presented in Fig. 1. The graph was plotted to estimate the slope which was then used to determine formaldehyde emission. The slope obtained 9.089 with \( R^2 = 0.997 \). The results showed that the admixture of urea in the resin imparted significant reduction of the FE levels (Fig. 2). The FE values for the Impreg without urea ranged from 80.89 to 172.2 ppm and the values greatly reduced to 8.70-15.3 ppm when treated with admixed urea followed by curing for 120 min. The FE increased with resin concentration and decreased with curing time. FE was found to be positively correlated (\( R = 0.897 \)) with polymer loading as described by WPG (Fig. 3). The results reflect that the reactive urea bonded...
with the free formaldehyde released by some of the methyol groups from the resin and formed the UF cross-linked polymer. It was anticipated that if the curing time was prolonged, more polymerization of resin would occur resulting in lower FE (Amarullah et al., 2010) but the mechanical properties might adversely be affected due to the hydrolyses of the cellulose chain (Ashaari et al., 1990b).

The presence of cross-linked UF polymer was also apparent from the FTIR spectra of the impreg product (Fig. 4). At the spectral area of 3700-3000 cm⁻¹, it indicated the difference between the pre-polymers and cured resin (Zobra et al., 2008) and the absorbance peak for the cured UF was at 3350 cm⁻¹ due to the formation of bonded NH group. Our study showed that this peak was at 3339 cm⁻¹. The formation of cross-linked polymer of PF was proven by the absorbance peak of 1234 cm⁻¹. Poljansek and Krajnc (2005) found that the absorbance bands which corresponded with the PF resin was 1235 cm⁻¹ for the asymmetric stretch phenolic C-OH. The excess free formaldehyde was still available in the treated wood as indicated by the absorbance peak of 2890 cm⁻¹ and this was comparable to 2914 cm⁻¹ (Poljansek and Krajnc, 2005) which is the characteristic peak of methyl group C-H.

**Properties of impreg:** Table 1 summarizes the analysis of variance (ANOVA) for the effect of resin concentration and curing at p<0.05. The descriptive statistics of the
Table 1: A summary of the analysis of variance (p<0.05) for the effects of concentration of MsavPF and curing time

<table>
<thead>
<tr>
<th>Variables</th>
<th>df</th>
<th>Density</th>
<th>WPG</th>
<th>MOR</th>
<th>MOE</th>
<th>ASE</th>
<th>WA</th>
<th>TS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (C)</td>
<td>2</td>
<td>0.906</td>
<td>0.576</td>
<td>0.173</td>
<td>0.028</td>
<td>0.382</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Curing time (CT)</td>
<td>2</td>
<td>0.906</td>
<td>0.007</td>
<td>0.077</td>
<td>0.126</td>
<td>0.551</td>
<td>0.000</td>
<td>0.002</td>
</tr>
<tr>
<td>C x CT</td>
<td>4</td>
<td>0.747</td>
<td>0.913</td>
<td>0.173</td>
<td>0.333</td>
<td>0.179</td>
<td>0.012</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Table 2: Mean on density, weight percent gain, and mechanical properties (+ standard deviation) of Impreg jelutong at different treatment combinations

<table>
<thead>
<tr>
<th>PF conc. (%)</th>
<th>Curing time (min)</th>
<th>Density (kg/m³)</th>
<th>WPG (%)</th>
<th>MOR (Nm²/m³)</th>
<th>MOE (Nm²/m³)</th>
<th>ASE (%)</th>
<th>WA (%)</th>
<th>TS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>60</td>
<td>630±127.0³</td>
<td>84.13±9.81⁴</td>
<td>79.40±7.65⁵</td>
<td>8255±34.5⁶</td>
<td>28.26±5.85⁷</td>
<td>43.56±2.19⁸</td>
<td>2.00±0.80⁹</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>59±121.4³</td>
<td>64.31±25.3⁶</td>
<td>80.70±16.0⁷</td>
<td>9579±20.8⁸</td>
<td>27.67±10.9⁹</td>
<td>38.19±2.12⁸</td>
<td>1.07±0.72⁹</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>583±46.8⁵</td>
<td>54.55±18.4⁶</td>
<td>77.73±8.38⁷</td>
<td>8903±47.2⁸</td>
<td>35.39±10.6⁹</td>
<td>36.82±2.65⁸</td>
<td>0.81±0.45⁹</td>
</tr>
<tr>
<td>30</td>
<td>60</td>
<td>54±55.8³</td>
<td>85.31±10.4⁶</td>
<td>70.31±15.5⁷</td>
<td>7752±23.7⁸</td>
<td>14.92±3.2⁹</td>
<td>55.88±2.38⁸</td>
<td>3.01±0.38⁹</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>690±24.0⁴</td>
<td>75.03±4.6⁶</td>
<td>80.90±12.6⁷</td>
<td>8744±89.6⁸</td>
<td>15.84±1.5⁹</td>
<td>33.75±1.48⁸</td>
<td>2.71±0.33⁹</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>649±28.4⁴</td>
<td>68.55±2.4⁷</td>
<td>69.98±5.0⁸</td>
<td>8442±91.0⁹</td>
<td>14.02±6.7⁹</td>
<td>26.64±1.01⁸</td>
<td>1.80±0.56⁹</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>79±13.9⁴</td>
<td>91.06±11.0⁸</td>
<td>80.71±6.3⁹</td>
<td>9192±83.4⁹</td>
<td>17.94±15.9⁹</td>
<td>24.72±3.7⁹</td>
<td>2.85±1.0⁹</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>759±32.1⁴</td>
<td>80.93±6.8⁹</td>
<td>78.57±7.0⁹</td>
<td>8983±85.9⁹</td>
<td>25.98±14.1⁹</td>
<td>20.55±4.6⁹</td>
<td>1.52±0.6⁹</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>698±34.1⁴</td>
<td>77.51±4.2⁹</td>
<td>83.92±4.2²</td>
<td>10432±114.5⁹</td>
<td>14.41±10.6⁹</td>
<td>19.11±3.0²</td>
<td>2.51±0.6⁹</td>
</tr>
<tr>
<td>Untreated solid wood</td>
<td>90</td>
<td>396±32.0⁹</td>
<td>62.95±4.7⁹</td>
<td>612±486⁸</td>
<td>-</td>
<td>631753.5⁴</td>
<td>4.18±1.1⁸</td>
<td></td>
</tr>
</tbody>
</table>

Group means with the same letter are not significantly different at p<0.05.

Fig. 5: The effect of weight percent gain (WPG) on the density of impreg jelutong

The increase in strength and stiffness. This phenomenon has also been reported by many researchers (Deka et al., 2000; Kajita and Imamura, 1991).

Dimensional stability of impreg: The dimensional stabilization of the impreg was quantified by analyzing the anti-swelling efficiency (ASE), water absorption (WA) and thickness swelling (TS). The untreated samples were used for comparison purposes. The ASE values were 27.7-35.4% for the wood treated with 20% resin, 14.0-15.8% for the treated wood with 30% resin and 14.4-26.0% for those treated with 40% resin. The ASE values indicated that some of the resin had successfully penetrated into the cell wall and upon heating, it formed an insoluble polymer which bulked the cell wall (Olmacı et al., 2002). At lower PF concentrations, more resin would penetrate into the cell wall and as a result, higher ASE values would be achieved compared with those treated at higher concentrations. The ASE for the impreg was markedly lower compared with the wood
treated without the admixture of urea reported in the previous study. Aikfei (2010) found that mahang (Macaranga spp.) impregnated with the same resin without the formaldehyde scavenger had an ASE value of more than 60%. Rowell (2005) revealed that the molecular weight distribution of the resins significantly influenced the viscosity and the ability of the resin to penetrate the cell wall. The presence of urea would have increased the molecular weight of the resin system, thus limit the penetration into the cell wall of the treated wood.

Lower WA (19.91-43.6%) was also found for the impreg compared with the untreated wood (63.2%). Among the treatment combinations, regardless of the curing time, the impreg produced from 40% resin had the lowest WA. This showed that at this concentration, the treating solution had a higher molecular weight distribution, thus limited the penetration into the cell wall and in turn, higher amounts of resin filled up the lumen and formed internal coating which reduced water absorption.

Resistance of impreg against fungal decay: The weight loss (WL) among the impreg after 12 weeks of exposure to the white rot fungus (Pycnoporus sanguineus) can be seen in Fig. 8. The impreg experienced lower WL compared with the untreated wood, that was 0 to 4.8% for the impreg and 18.4% for the untreated wood. It was also found that WL decreased with the increase of concentration and curing time. The findings showed that the impregnation treatment with the presence of urea had successfully increased the resistance of jelutong impreg against fungal decay by 80-100%. Earlier research revealed that polymer loading of 30% was enough to protect Macaranga sp. impreg from white rot (Aikfei, 2010) and at resin weight gain of 10-20% was enough to suppress the growth of decay fungi (Furuno et al., 2004).
CONCLUSIONS

Impregnation of low density wood *Dyera costulata* with admixture of urea (30% based on solid PF resin) was able to reduce formaldehyde emission from the products. The FTIR spectra analyses showed that urea had reacted with some free formaldehyde and formed a cross-linked UF polymer. Regardless of PF concentration, the formaldehyde emission decreased as the curing time increased. The lowest formaldehyde emission was found on the impreg cured at 150°C for 120 min. The impreg had higher MOR, MOE and dimensional stability compared to the untreated solid wood. The analysis of variance showed that the concentration of resin (C) significantly affected the density, MOE, WA and TS while curing time (CT) affected the density, WPG, WA and TS. There was no interaction between C and CT for all properties tested. The treatment rendered the impreg products with approximately 20% in ASE. Besides, the moisture uptake and thickness swelling of the impreg were lower compared to the untreated wood when exposed to high humidity over a period of time. The treatment had also changed the wood into highly resistant to fungal decay.

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