Polymerised merbau extractives as impregnating material for wood properties enhancement

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Abstract. This study aimed to investigate the polymerisation process of Merbau extractives (ME) and the characteristics of the phenolic resin polymers made from ME. These polymerised ME (PME) can potentially be utilised as an impregnating material to enhance the wood properties of young plantation timber. Selected PME were characterised via Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry, thermogravimetric analysis, X-ray diffraction analysis, and ultraviolet-visible analysis. The prediction of the enhancement to the wood properties when treated with the obtained PME was discussed in relation to the physico-chemical and thermal characteristics of the polymeric materials. The results showed that the ME can be polymerised in its base condition with formaldehyde and resorcinol as the copolymer to produce the PME. The resin was classified as a resole and polymerisation can be done at room temperature. The physico-chemical tests and analyses, via boiling tests and FTIR spectra confirmed that the polymeric compound is a promising impregnating material that can enhance wood properties. This polymeric material is also eco-friendly as the low level of free formaldehyde.

1. Introduction

Merbau extractives (ME) have been shown to be a promising material for the enhancement of wood properties because of their high content of phenolic compounds, particularly resorcinol (R) [1]. A phenolic resin has been successfully made from ME in the past and used as an adhesive through polymerisation with the addition of a small quantity of R and formaldehyde (F) at a ME:R:F ratio of 100:5:10 (w/w). The adhesive quality fulfilled the exterior requirements [2]. Future research could determine if a similar formulation can be used to develop a wood impregnating material because of the initial hydrophilic nature of ME in an aqueous solution and it becoming water-insoluble or hydrophobic as a reaction proceeds, which occurred with the ME adhesive.

A phenolic resin is a compound that contains a wide variety of materials based on a broad range of phenols (P) and co-monomers [3]. Phenolic resins are obtained via a reaction of P and aldehydes. Both parent compounds, P and F, are by far the most important components in the production of commercial phenolic resins [4]. Phenolic resins are known to be a versatile resin system that feature either a stable, thermoplastic novolak composition that is cured with a latent source of F (hexa) or a heat reactive and perishable resole composition that is cured either thermally or under acidic or special basic conditions [5, 6]. Until the end of the 19th century, P was recovered primarily from coal tar. Phenolic resin was
one of the first synthetic resins used commercially, both in plastics and surface coatings [7]. With the commercialisation of phenolic resins, the demand for P has grown remarkably. Currently, the cumene-to-P process, which is an industrial process for developing P and acetone from benzene and propylene, is the predominant synthetic route for the production of P [8].

There has been an increasing demand for natural products in industrial applications in recent years because of environmental issues, waste disposal, and depletion of non-renewable resources. These concerns encourage researchers to develop phenolic resins from renewable resources or bio-based phenolic resins [9]. According to Manjula et al. [10], the utilisation of renewable resources for polymer applications has been the source of much discussion since the early 1980s. This is partly because of the recognition that petroleum and coal supplies are limited and that the cost of petrochemicals is on the rise. Thus, biomass, which consists mostly of polymers and monomers, is a suitable renewable resource. The work of Manjula et al. [10] resulted in the successful creation of a novolak resin from 33.8 g (0.16 mol) of coconut shell tar that was mixed with 10.38 mL of a 37% aqueous solution (0.128 mol F and 1 g of oxalic acid) by stirring in a water bath at 100°C for 5 h. A vacuum was then applied to remove water via condensation. The yield of the phenolic resin was found to be 97%.

Lignocellulosic wastes (sawdust and cornstalks) have been converted to produce phenolic compounds that may be suitable for the production of green PF resins via direct liquefaction in hot-compressed water at temperatures of 250°C to 350°C in the presence of 2 MPa H2 [11]. Phenolic resins are formed by either alkaline or acid catalysis, with the addition of F to P to give ortho- and para-substituted products. The properties of these products depend largely on the catalyst and P/F molar ratio. In resole formation, the excess F is reacted with P under basic conditions [5].

This paper aimed to investigate the polymerisation process of ME and the characteristics of phenolic resin polymers made from ME, further classified as polymerised ME (PME) that can be potentially utilised as an impregnating material to enhance wood properties.

2. Materials and Methods
2.1. Material
In the previous study [1], ME were obtained from a Merbau wood powder extraction using hot water. Similar procedures to produce the crude ME were used in this study for the polymerisation process to produce the impregnating material PME. In the polymerisation process, a technical grade R was used as an activating agent, 37% F was used as a cross-linker or curing agent, and 40% NaOH was used as the catalyst. The ME primarily contained R with a molecular weight of 110.11 g/mol, while the molecular weight of F is 30.03 g/mol. As the R present in ME is not free R, but bonded in a complex compound, pure R was added to activate the extractives.

2.2. Methods
2.2.1. Polymerisation Process of ME
2.2.1.1. Determining the basic and experimental proportions of ME:R:F
To determine the optimal formula, a typical resole resin with a F/P molar ratio in the range of 2:1 to 2.5:1 [3] was made with a 4% to 8% alkali content. According to this ratio, the proportions for the resole formula consisted of 27.65% P, 35.28% F, and 4.71% NaOH. Previous ME:R:F compositions with a lower portion of F (10%) and R (5%) have been successfully made for adhesive purposes [2]. Because of the different purpose of this study, a recalculation was required to determine a new composition. For the basic calculation, 4000 mL (density = 1.13 g/mL) of a liquid ME:R:F mixture was taken for composing proportions with consideration given to the densities and molecular weights of all three materials (Table 1).
**Table 1.** Molecular weight proportion to determine the ME:R:F mixture composition

| Description                        | ME  | R   | F   |
|------------------------------------|-----|-----|-----|
| Density\(^a\) (g/cm\(^3\))        | 1.02| 1.29| 1.09|
| Molecular weight\(^b\) (g/mol)     | 110.11| 110.11| 30.3|
| Reference proportion (%)\(^c\)     | 85  | 5   | 10  |
| Proportion of 4000 mL basis volume | 3400| 200 | 400 |
| Weight (g)                         | 3468| 258.4| 436 |
| Molecular weight (g/mol)           | 31.50| 2.35| 3.96|
| Percent weight (wt.%)              | 83.32| 6.21| 10.47|
| Mole proportion                    | 1   | 0.1 | 0.2 |

\(^a\) ME from [1]; R from [11]; F from [12]

\(^b\) Molecular weight of ME was assumed as the same as R

\(^c\) [12]

Based on the percentages of F (10.47%) and R (6.21%), a range of combinations for both substances were added to the liquid ME for the polymerisation process. Both values were assumed to be the median. For simplicity, the range for F was from 0% to 20% with an interval of 5% and the range for R was 0% to 10% with an interval of 2.5% (Table 2).

**Table 2.** Combination of R and F with ME

| Proportion | F (%) | 0  | 5  | 10 | 15 | 20 |
|------------|-------|----|----|----|----|----|
| R (%)      | Code  | 1  | 2  | 3  | 4  | 5  |
| 0          | PME11 | PME21 | PME31 | PME41 | PME51 |
| 2.5        | PME12 | PME22 | PME32 | PME42 | PME52 |
| 5          | PME13 | PME23 | PME33 | PME43 | PME53 |
| 7.5        | PME14 | PME24 | PME34 | PME44 | PME54 |
| 10         | PME15 | PME25 | PME35 | PME45 | PME55 |

2.2.1.2. Polimerisation

Based on the F (0%, 5%, 10%, 15%, and 20%) and R (0%, 2.5%, 5%, 7.5%, and 10%) that were added into 100 mL of aqueous ME, there were 25 combinations for the PME mixtures, which are shown in Table 2. The mixture was stirred until the R was dissolved. As a catalyst, 40% NaOH solution was also added to the mixture to increase the pH from 5 to 6 to a pH of 10 to 11. According to Detlefsen [3], the base solution results in the polymer becoming aqueous soluble when it is strong enough and causes a salt to form, which is the source of activation. After a homogeneous mixture was formed, 10 mL of 37% F was added to the mixture. It was stirred again until a homogeneous solution was obtained. The addition of F is known as methylation, and in this study the derivative compound that was expected to form was hydroxymethyl-ME. The above procedure was applied for all of the compositions, PME11 to PME55, at room temperature. The compounds were then set out at room temperature for 24 h to make sure that the reaction was completed, which was when condensation or chain extension occurred. A visual check of all of the compositions was conducted every hour.

2.2.2 Testings

2.2.2.1. Polymer forming test

The three components are hydrophilic compounds, and they can change to a hydrophobic material after the polymerisation process when in the proper proportion. A polymer is formed when the mixture...
changes from a liquid phase to a gel or solid phase. To accelerate the polymerisation process, 20 g of each mixture was placed into a petri dish and then oven-dried at 100°C ± 2°C to form a glassy solid on the petri dish, which is shown in Figure 1. All of the oven-dried mixtures with solid phases were allowed to sit for 24 h at room temperature (28°C). The polymer was formed when the solid phase did not absorb water vapour from the surroundings.

2.2.2. Boiling test
To make sure that the PME were permanently formed, a boiling test was performed. All of the PME that passed the polymer forming test were boiled in water at 100°C for 4 h. The PME were determined to have permanently formed if they did not dissolve in the boiling water.

![Figure 1. PME mixtures: (a) polymer is not formed; (b) wet mixture after conditioning; oven-dried PME22 (c) and PME33 (d); (e) PME22 after the boiling test; and (f) PME33 after the boiling test](image)

2.2.2.3. Free formaldehyde test
Formaldehyde is commonly used as a cross linker or curing agent [2, 13, 14]. Ideally, this compound should react perfectly with R and the extractive. However, it is normal for a small amount of reactant to not react. Lower amounts of free F in the PME are better for the polymers.

The test procedure to determine the free F content was as follows [2]. The amounts 0 mL, 5 mL, 10 mL, 20 mL, 50 mL, and 100 mL of a standard 3-mg/L F solution were pipetted into six bottles (100 mL each), and then they were diluted by adding water up to the 100-mL line. Each bottle contained F concentrations of 0 mg/L, 0.15 mg/L, 0.3 mg/L, 0.6 mg/L, 1.5 mg/L, and 3 mg/L, respectively. Samples of liquid PME were diluted in water up to 100 tME, and then 10 mL of ammonium acetate (20%; 200 g in 1000 mL) were added into 10-mL PME samples, which was followed by 10 mL of acetyl acetone (0.4%; 4 mL in 1000 mL). All of the solutions were then put in a water bath at 40°C for 10 min and then
cooled until room temperature was reached. The solution was measured with a photometer (UV-Vis 1700, Shimadzu, Kyoto, Japan) at a wavelength of 412 nm.

2.2.2.4. Potlife test
All of the PME mixture formulations were stored in covered cups and the time taken for the phase to change from liquid to gel was recorded. It is known that the potlife time is longer when it takes longer for the gel to form [2, 15].

2.2.2.5. Solids content test
Determining the solids content followed the procedure by Sluiter et al. [16] with some modifications regarding the sample. The weight of the empty dishes was measured. Then, 20 mL of ME and the ME:R:F polymer were weighed together with the dishes and put in an oven at 105 °C ± 3 °C for 1 h. The dishes with the polymer were conditioned at room temperature, stored in desiccators, and then weighed. The samples were then oven-dried and weighed to reach a constant oven-dried weight. The total solids content (TSC) was determined with the following equation:

\[ \text{TSC} = \frac{(W_t - W_o)}{W_o} \times 100 \]  

where \( W_p \) (g) = weight of dish; \( W_o \) (g) = weight of polymer sample; and \( W_t \) (g) = \( W_p + \) polymer residue.

2.2.2.6. Selection of a proper PME composition
The selection of the PME composition was based on the results of the polymer testing using the following criteria:
   a. The polymer was formed when the mixture changed from a liquid phase to a gel or solid phase after conditioning.
   b. The formed polymer was hydrophobic, and therefore it did not absorb water from the surroundings during conditioning at room temperature.
   c. The polymer was not dissolved in boiling water (100 °C) after 4 h during the boiling test.
   d. The amount of free F was less than 1%.
   e. The potlife was greater than 18 h.

2.2.2.7. Fourier Transform Infrared Spectroscopic Analysis
Fifteen milligrams of PME from the selected samples (120 Mesh size) were directly taken for the FTIR spectroscopic analysis. The dried powder samples were taken from the PME samples, which represented formed and unformed polymers. They were then embedded in KBr pellets and analysed using a MB3000 spectrometer (ABB, City, Canada). They were scanned via the absorption mode in the range of 4000 cm\(^{-1}\) to 500 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\).

3. Results and Discussion

3.1. ME polymerisation
The ME polymerisation is a process conducted on ME to form a polymer or resin that can be used for impregnating materials. When another component is added into the mixtures or an attempt is made to reduce the main component of the mixtures, this is referred to as modification of the phenolic resins [17]. In the current study, ME was used as the component addition, as well as for reducing the main component in the resin formulations, \( \text{i.e., R} \). Furthermore, reducing the R levels also means reducing the F levels. A RF-resin can be easily synthesised via the poly-condensation of R and F in an aqueous solution and the structure of the resulting resins with a base [1819].

In general, the reaction between R and F at basic catalysation conditions results in methylol R (Figure 2) [11]. Formaldehyde addition is known as methylation [3, 11]. In the current study, the derivative compound that was expected to form was hydroxymethyl-ME.
The addition of a 40% NaOH solution as the catalyst forms a salt that is the source of activation. Referring to phenolic resins manufacturing, the salt has an enhanced electron density at the reactive ring positions. This is the source of activation [3]. In the current study, the reason R was treated with NaOH for ME polymerisation was to form the activated salt (Figure 3). The polymerisation process was base catalysis using NaOH, and so the pH increased (Table 3).

**Figure 3.** R activation by NaOH

The pH values of the ME and selected PME (i.e., PME22 and PME33) are presented in Table 3. The pH of the PME doubled from 5.4 to approximately 10 to 11.

**Table 3.** pH of the crude ME and PME

| Sample  | pH at Measuring Time (h) |
|---------|--------------------------|
|         | 0    | 1    | 3    | 5    | 8    | 12   | 24   |
| ME      | 5.4  | 5.4  | 5.4  | 5.4  | 5.3  | 5.4  | 5.2  |
| PME22   | 10.3 | 10.6 | 10.5 | 10.4 | 10.8 | 10.5 | 10.2 |
| PME33   | 10.2 | 10.9 | 10.9 | 11.0 | 10.6 | 10.4 | 10.3 |

In addition to the provision of an aqueous solution and salt formation, manufacturing phenolic resins in a strong base with a very high pH (above 10) results in an increased gelation time [20]. Having a high pH could also prevent an extreme decrease in the resin pH when it comes in contact with wood during impregnation. The pH of the resin might decrease when the resin comes in contact with acids in wood [21].

The addition of F results in methylation [3,11]. The methylation and following reactions for ME polymerisation can be predicted by following the formation of resorcinolic resins from the RF reactions that generally take place in three stages, which are shown in Figure 4 [11]. The first step of the RF reaction is an addition reaction, where R combines with F to form hydroxymethyl (or methylol) R.
the second step, after methylation, the condensation of the methylol group occurs, which forms methylene and methylene ether (or benzyl ether) bridge structures. The last step is the disproportionation reaction in which the benzyl ether structures are decomposed to produce the methylene bridged structures and F. This is the reason why excess or free F emissions occur.

**Figure 4.** RF resin formation from the RF reaction

### 3.2. PME formation

Based on the results of the ME polymerisation process, which created 25 combinations of R and F polymers, and the data from the test results of all of the PME combinations, six different groups of PME formations were classified, which are as outlined below and summarised in Figure 5. The PME groups are as follows:

(a) **Group 1:** The polymers were not formed, as the mixture was still in the liquid phase after being conditioned at room temperature for 24 hours. These polymers had neither R nor F added to the mixtures. These polymers were PME11, PME21, PME31, PME41, PME51, PME12, PME13, PME14, and PME15.

(b) **Group 2:** The polymers were still wet after they were oven-dried and conditioned for 24 hours at room temperature because they absorbed water vapour from the surroundings. These polymers were PME23, PME24, and PME25.

(c) **Group 3:** The polymers were dissolved in hot water (80°C) after boiling for 4 hours. These polymers were PME34, PME35, and PME45.

(d) **Group 4:** The polymers were formed and were resistant to the boiling test. However, the level of free F produced was greater than or equal to 1%. These polymers were PME32, PME42, and PME52.

(e) **Group 5:** The polymers were formed and were resistant to the boiling test. The level of free F produced was less than 1%, but the storage time was less than or equal to 18 hours. These polymers were PME43, PME44, PME53, PME54, and PME55.

(f) **Group 6:** The PME fulfilled all of the criteria of Group 5, except they had a storage time greater than 18 hours. These polymers were PME22 and PME33.

The first step of ME polymerisation is the addition of R to the ME to activate the R contained in the complex compound of the extractives. Although the ME content is predominately R [1], the R is still bonded in the complex compound of the extractives. The addition of only R did not result in resin or
polymer formation because methylation did not occur. As a result, polymers were not formed for PME12, PME13, PME14, or PME15 (Group 1). The addition of F is required for the second stage of polymerisation to occur. The addition of only F into the aqueous ME also did not lead to resin formation, as was shown by PME21, PME31, PME41, and PME51 (Group 1). Based on the physical characteristics investigated during the polymerisation process, the Group 6 polymers (PME22 and PME33) could be recommended for use as an impregnating material for wood.

| F (%) | 0   | 5   | 10  | 15  | 20  |
|-------|-----|-----|-----|-----|-----|
| R (%) | Code| 1   | 2   | 3   | 4   | 5   |
| 0     | 1   | PME11| PME21| PME31| PME41| PME51|
| 2.5   | 2   | PME12| PME22| PME32| PME42| PME52|
| 5     | 3   | PME13| PME23| PME33| PME43| PME53|
| 7.5   | 4   | PME14| PME24| PME34| PME44| PME54|
| 10    | 5   | PME15| PME25| PME35| PME45| PME55|

![Figure 5. Block graph of the PME compositions](image)

3.3. Effect of the F/R ratio

The reaction of F with P can lead to either a heat reactive resole or a stable novolak and is dependent upon the mode of catalysis and the F/P molar ratio [4]. The mixtures of ME, R, and F found in Group 2 still showed similar properties to those of the original components of the mixtures, i.e., hydrophilic or water soluble. This indicated that polymers were not formed. The ME is water soluble and can easily leach out from wood, which can lead to problems during wood processing. As a result, the extractive is easily extracted, even with only cold water. Resorcinol is also highly soluble in water [11]. To ensure the mixture remains hydrophobic, it should be polymerised with a proper R/F ratio, or the mixture will return to its initial properties, i.e., hydrophilic.

Regarding the R/F ratio, Figure 5 shows that in Group 2, the proportions (%) of R/F were 5:5, 7.5:5, and 10:5 for PME23, PME24, and PME25, respectively. When these proportions were converted to a molar ratio, they were 1:0.59, 1:0.4, and 1:0.3, and the F/R ratios were 0.59, 0.40, and 0.30, respectively. This meant the R/F molar ratios were greater than 1. This was the reason why there was no polymer formation with these three mixtures. To make the mixtures polymerise at room temperature without heat treatment, the R/F molar ratio should be less than 1 or the F/R ratio should be greater than or equal to 1 [4,11]. These resins are classified as resoles [3,4,11,21]. Table 4 shows the molar ratios for all of the combinations of F and R added to the liquid ME in this study.

| F (%) | 0   | 5   | 10  | 15  | 20  |
|-------|-----|-----|-----|-----|-----|
| R (%) | Code| 1   | 2   | 3   | 4   | 5   |
| 0     | ~a  | ~a  | ~a  | ~a  | ~a  |
| 2.5   | 0b  | 1.19f| 2.37d| 3.56d| 4.74d|
| 5     | 0c  | 0.59b| 1.19f| 1.78e| 2.37e|
| 7.5   | 0d  | 0.40b| 0.79e| 1.19e| 1.58e|
| 10    | 0e  | 0.30b| 0.59c| 0.89e| 1.19e|

Remarks: a, ..., f = Group 1, ..., Group 6 refers to Figure 5

Lower F/R ratios resulted in the PME failing the boiling test. The results indicated that PME34, PME35, and PME45 from Group 3 were dissolved in hot water. The F/R molar ratios for the three compositions were less than 1, i.e., 0.79, 0.59, and 0.89, respectively. This meant that polymers were
not formed for these three mixtures. Their solid states after the accelerated heating process were not permanent because of the high concentration of the mixture. The F concentration in the mixtures was not enough to function as the cross-linker. Possible polymerisation involving R and ME is indicated when no extractive is extracted after hot water treatment [2]. In contrast, the F/R ratio in Group 4 was much higher compared with the ratios of 2.37, 3.56, and 4.74 for PME32, PME42, and PME52, respectively. For these resins, the excess F was probably too high and resulted in free F levels of more than 1%. According to SNI 06-4567-1998 [22], free F levels are categorised as low if they are less than 1%.

The combination of R and F in the ME for PME43, PME44, PME53, PME54, and PME55 in Group 5 had a positive effect on polymer formation and the resistance to hot water, and resulted in low levels of free F. However, the storage time was shorter than 18 h, which was lower compared with the two formed resins PME22 (35 hours) and PME33 (28 hours). Additionally, the usage of R and F in Group 5 was higher than in the last two polymerised ME (Group 6).

The storage life is affected by the P/F ratio and pH [23]. Phenolic resins that are prepared via basic catalysts tend to have shorter storage lives than those prepared via an acidic process. Also, the lower portion of F in the resin resulted in a longer storage life. The storage lives for the resin with initial P/F ratios of 1:0.73 and 1:0.66 were 4 d to 5 d and 6 d to 7 d, respectively. In contrast, the portion of F must be higher than that of R (F/R greater than or equal to 1) so that polymerisation can occur at room temperature.

Table 4 shows the F/R ratios. It was observed that resins or polymers were formed with the ME mixtures when R and F were added to the aqueous ME with a F/R ratio greater than 1. The addition of F resulted in methylation [3]. The methylation and following reaction in the ME polymerisation process can be predicted by following the formation of resorcinolic resins from the RF reactions, which is shown in Figure 4.

3.4. Solids content

The TSCs of the crude ME and two selected PME (PME22 and PME33) are presented in Figure 6. It was observed that PME33 had a higher TSC than PME22 because a higher proportion of the active compounds was added (5% R and 10% F), although the F/R ratios were the same (1.19), which is shown in Table 4.

![Figure 6. Total solids content of the crude ME and two selected PME](image)

The solids content influences impregnated lignocellulosic materials, such as wood and rattan. Utilising the ability to alter the solids content, the weight gain and density of the impregnated material can be improved, as well as other properties of the impregnated material. A higher solids content improves the anti-shrink efficiency, specific gravity, hardness, and nail withdrawal of wood [24].
3.5. FTIR spectra

Figure 7 and Table 5 show the FTIR spectra and band assignments of the peaks of the formed PME (PME22, PME33, PME44, and PME55), unformed PME (PME34, PME35, and PME45), and a formed PME with a free F greater than or equal to 1% (PME52). The spectra of PME22, PME33, PME44, and PME55 show relatively similar peak patterns. The FTIR spectra showed a broad absorption peak at approximately 3400 cm\(^{-1}\), which could have been a stretching vibration of the hydroxyl linkage between the phenolic groups that appeared in all of the mixtures, as the major components of the ME are phenolic compounds [1]. However, it was obvious that the polymerisation of the ME caused the intensity of the OH absorption band (approximately 3400 cm\(^{-1}\)) to decrease by 22%, 31%, 44%, and 47% for PME33, PME22, PME44, and PME55, respectively, which were smaller compared with the 59%, 82%, and 86% decreases for PME35, PME34, and PME45, respectively. These decreases revealed that the hydroxyl group content was reduced after the polymerisation process. Furthermore, the reduction in the hydroxyl group content can explain why an improvement in the dimensional stability of the impregnated wood using the selected formed PME occurred. This reduction was caused by the occurrence of cross-linking reactions [25,26]. Therefore, it can be stated that the decrease of less than 20%, which occurred for PME52, was because of the higher F content, which can initiate cross-linkage.

![Figure 7. FTIR spectra of the PME: a) formed PME; and b) unformed and formed PME with a higher proportion of F/R](image-url)

There were apparent differences between the two groups of PME (formed and unformed) with respect to the presence of the absorption bands of CH, CH\(_2\), or CH\(_3\) stretching in the methyl and methylene groups at 2924 cm\(^{-1}\) in the formed PME. This could have been because of the polymerisation process that occurred in the ME after the methylation stage (Figure 4), in which condensation of the methylol group occurred to form methylen and methylene ether bridge structures [11,27]. A noticeable difference also occurred because of the existence of the alkyne (C≡C) peak in the formed PME group at 2100 cm\(^{-1}\) to 2260 cm\(^{-1}\). The peak associated with the C≡C structure is characteristic of the impact on
the carbon-carbon bond stretching as an increasing function of the bond order for the series of single-, double-, and triple-bonded carbons [27]. This increase in the bond order produced a corresponding increase in the bond strength. As a result, it was concluded that the PME were bonded strongly and would not be leached out during the boiling test and the colour of impregnated wood would not be altered because of cross-linking between the PME and wood during curing. The existence of the functional groups that reacted with wood could improve the wood fixation or anti-shrinkage because of the hydrophobicity of the polymeric material. Cross-linking may be achieved via reactions with the functional groups [21].

The peak from 1600 cm\(^{-1}\) to 1650 cm\(^{-1}\) was identified as a prominent and strong C=C stretching absorption of an aromatic ring in the synthesised resins [28]. This typical peak indicated the presence of R because this compound is conjugated by two functional groups of OH and one aromatic ring of C=C. The aromatic aldehyde and CH deformation in the polymers appeared with small differences in the intensities of the absorption bands amongst both PME groups from 1300 cm\(^{-1}\) to 1475 cm\(^{-1}\). In the fingerprint area, the peaks represented ester CO groups at 1000 cm\(^{-1}\) to 1300 cm\(^{-1}\) and out-of-plane bending of alkene CH groups from 600 cm\(^{-1}\) to 1000 cm\(^{-1}\), which were in all the spectra. The presence of carboxylic acid esters, anhydrides, amides, and carbonates in the polymeric resin could be a special resole curing system that could accelerate the curing of resole resins [29].

**Table 5.** Peak assignments of the FTIR spectra of selected PME [26, 27, 30-32]

| Wavenumber (cm\(^{-1}\)) | Band assignment                                      |
|---------------------------|------------------------------------------------------|
| PME22 3456 PME33 3441    | Hydroxyl functional groups (OH) stretching           |
| 3418 3448 3441 3441       | C–H and CH\(_2\) stretching in methyl and methylene |
| 3448 3441 3441 3441       | groups                                               |
| 2924 2924 2924 2924       | Alkynes (C≡C)                                        |
| 2129 2122 2114 - - - -    | Carbonyls (CO)                                       |
| 1713 1713 - - - - - 1744 | Alkenes (C=C; Aromatic ring)                         |
| 1643 1643 1636 1636 1643 | Aromatic aldehyde; C–H deformation in polymers      |
| 1628 1643 1643 1643 1643 | Esters groups (C-O-)                                 |
| 1456 1381 1466 1466 1458 | Alkene (C-H-) out-of-plane bending                   |
| 1458 1458 1458 1458 1458 |                                                       |
| 1180 1219 1296 1296 1219 |                                                       |
| 1088 1219 957 972 949     |                                                       |
| 849 849 764 725 957       |                                                       |

3.6. Free formaldehyde

Because of global concerns about the health, safety, and environmental sustainability of phenolic resins, the effects of manufactured products that use these resins should be considered. Resole usually has excess aldehyde [3]. The manufacturing of PF resins, or any phenolic resin, could potentially jeopardize such an undertaking of developing an environmentally sustainable resin on both the laboratory and manufacturing scales with several levels of hazards. The hazards come from components or monomers that may be highly toxic, flammable, or corrosive to the human body. However, the resins themselves are generally rated as non-dangerous because of the excess F, as shown in the reaction above. Nevertheless, environmental factors should be considered.

**Table 6.** Concentrations of the standard F and absorbent

| Standard F (ppm) | 0 0.050 0.100 0.200 0.300 0.400 0.500 |
|------------------|----------------------------------------|
| Absorbent (ppm)  | 0 0.082 0.171 0.380 0.596 0.818 1.034 |
Table 7 shows the measurement results of the free F based on the standard for F absorption at selected concentrations (Table 6) via a photometer at a wavelength of 412 nm. The relationship between the concentration \((X)\) and absorbent \((Y)\) was expressed by:

\[
Y = 2.0927X - 0.0232 \tag{3}
\]

The \(R^2\) was 0.9987 (Figure 8). Therefore, this expression was reliable for calculating the F concentration in the samples.

![Figure 8. Concentration of the standard and absorbent](image)

**Table 7. Absorbent and F concentration in the tested samples**

| Sample   | Absorbent 1 (ppm) | Absorbent 2 (ppm) | Average (ppm) | Concentration (ppm) |
|----------|-------------------|-------------------|---------------|---------------------|
| PME22    | -0.005            | -0.005            | -0.005        | 0.009               |
| PME23    | 0.003             | 0.003             | 0.003         | 0.013               |
| PME24    | 0.000             | 0.001             | 0.001         | 0.011               |
| PME25    | 0.001             | 0.001             | 0.001         | 0.012               |
| PME32    | 0.019             | 0.020             | 0.020         | 0.020               |
| PME33    | -0.001            | -0.001            | -0.001        | 0.011               |
| PME34    | 0.007             | 0.007             | 0.007         | 0.014               |
| PME35    | 0.000             | 0.000             | 0.000         | 0.011               |
| PME42    | 0.020             | 0.020             | 0.020         | 0.021               |
| PME43    | 0.010             | 0.010             | 0.010         | 0.016               |
| PME44    | -0.001            | -0.001            | -0.001        | 0.011               |
| PME45    | -0.001            | -0.001            | -0.001        | 0.011               |
| PME52    | 0.035             | 0.035             | 0.035         | 0.028               |
| PME53    | 0.016             | 0.016             | 0.016         | 0.019               |
| PME54    | 0.010             | 0.010             | 0.010         | 0.016               |
| PME55    | 0.005             | 0.005             | 0.005         | 0.013               |

In this study, the level of free F was considered to be one of the selection criteria for the PME formulation, with an extremely low level of maximum free F at 0.01 ppm. Table 9 shows that the lowest free F was 0.009 ppm (PME 22) and the second lowest was 0.011 ppm (PME24, PME33, PME35, PME44, and PME45). Based on the free F values, the polymerised ME that can be considered for use as an impregnating material were PME22 and PME33. PME33 also has other advantages that were explained previously. Free F and free P are the components that cause toxicity in phenolic or aldehydic synthetic resins. In general, PF resins with a low toxicity have poor bond strengths, while a great bonding strength is often accompanied by a high toxicity [33]. This study expected there to be no effect from lower free F levels on the bonding strength between the PME and impregnated wood.
4. Conclusion

Merbau extractives can be polymerised in basic conditions with F and R added as the copolymer to produce PME. The resin is classified as a resole because the R/F molar ratio should be less than 1 or the F/R ratio should be greater than or equal to 1, so that polymerisation can occur at room temperature. The results of the physico-chemical tests and analysis via FTIR spectroscopy confirmed that the polymeric compound is a promising impregnating material for the enhancement of wood properties. This material is also eco-friendly since extremely low level of free formaldehyde.

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