The Use of Environmentally Friendly Bio-Oil in the Production of Phenol Formaldehyde (PF) Resin

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ABSTRACT

Phenol Formaldehyde (PF) resin has been extensively used in the manufacturing industry as a binding agent, especially in the production of wood-based panels because of its ability to provide good moisture resistance, exterior strength and durability as well as excellent temperature stability. However, due to the use of limited petroleum-based phenol in its formulation, there is a strong interest in exploring renewable biomass material to partially substitute the petroleum-based phenol. In this study, the slow pyrolysis of biomass decomposition process was used to convert two types of biomass, namely, oil palm frond and *Rhizophora* hardwood, into bio-oil. The phenol-rich fraction of the bio-oil was separated and added into the formulation of PF resin to produce an environmentally-friendly type of PF resin, known as bio-oil-phenol-formaldehyde (BPF) resin. This BPF resin was observed to have comparable viscosity, better alkalinity, improved non-volatile content and faster curing temperature than conventional PF resin. Moreover, the particleboard bonded with this BPF resin was observed to have just as excellent bonding strength as the one bonded using conventional PF resin. However, the BPF resin exhibited an increased level of free formaldehyde and less thermal stability than the conventional PF resin, probably due to the addition of the less reactive bio-oil.

Keywords: Phenol formaldehyde resin, bio-oil, oil palm frond, *Rhizophora* hardwood

INTRODUCTION

PF resin, also known as phenolic resin, is a reddish-brown resin mainly produced from condensation reaction of petroleum-based phenol and excess formaldehyde. The reaction is also catalysed by an alkali to produce resole-type resin (Athanassiadou et al., 2002). The resole, frequently in liquid form, can be cured to a solid thermosetting network polymer using heat.

PF resin is extensively used in the manufacturing industry for production of moulding forms, thermo-insulation materials, rubbers, laminates as well as abrasive and frictional materials in which the resin acts as a binding agent. PF resin is also used as a binding agent in composite wood panels or wood-based panels such as particleboards, fibreboards, plywood and orientated strand boards (OSB). The latter application represents the major application segment of PF resin, with over 34% of the total volume production. In 2014, approximately 4.7 million tons of PF resin was produced globally, especially in the Asia-Pacific region, which consumed around 35% of the global consumption. In terms of revenue, the production of PF resin was valued at approximately USD10 billion in 2014 and is expected to reach approximately USD14 billion by 2020 (Zion Research, 2015).

As a matter of health concern, there are two potential sources of formaldehyde emission from composite wood panels or wood-based panels, namely, the unreacted free formaldehyde from synthesis of PF resin and the formaldehyde release resulting from breakdown of cured resin. The release of unreacted free formaldehyde from the panels can be greatly limited by controlling the formaldehyde to phenol molar ratio during resin production. In the case of PF resin, the amount of free formaldehyde has been reported as undetectable (Chaouch et al., 2014; Cheng et al., 2011; Shakhreet et al., 2013).

A potentially greater source of formaldehyde emission comes from the chemical breakdown of cured resin, known as hydrolysis, which usually occurs in the presence of water. However, it was reported that panels bonded with PF resin emit nearly no formaldehyde (Shakhreet et al., 2013). This is because PF resin tends to be more chemically stable than other formaldehyde-based resin such as urea formaldehyde (UF) resin or melamine-urea formaldehyde (MUF) resin. Furthermore, the chemical structure of cured PF resin is less hydrophilic towards water, which contributes to the fact that PF resin has good moisture resistance. The two characteristics make cured PF resin much less susceptible to hydrolysis that will induce formaldehyde emission. In both the United States and Europe, panels bonded with PF resin are classified as non-emitting and are exempted from formaldehyde emission regulations (Böhm et al., 2012).

However, the main drawback of conventional PF resin is that it can be very expensive due to the price of phenol. Hence, the use of more natural products such as bio-oil has been utilised. Bio-oil is a very suitable option because it is rich in phenols, which are mainly found within the bio-oil in the form of pyrolytic lignin (Kim et al., 2010).

Several attempts have been made to utilise bio-oil as a phenol substitute to produce BPF resin. These attempts include the incorporation of bio-oil obtained from fast pyrolysis of pine wood (Sukhbaatar et al., 2009), direct liquefaction of white pine sawdust (Cheng et al., 2011) as well as fast pyrolysis of white spruce and trembling aspen (Chaouch et al., 2014). From there, it was noticed that all of the available literature reported on the use of bio-oil originating from softwood biomass, probably because softwood contains a relatively higher content of lignin than any other types of biomass, and in turn, promotes the production of bio-oil with a higher amount of phenols (Demirbas, 2010).

This study was conducted to describe the area still unexplored in research related to the synthesis of BPF resin originating from non-softwood biomass, oil palm frond and *Rhizophora* hardwood. The rationale behind the selection of oil palm frond was due to its abundant availability across the world. Oil palm frond is usually harvested annually at about

10.9 tons per hectare from more than 13.5 million hectares of oil palm plantation around the world. Since oil palm frond has a very limited utility, an initiative was taken by this study to optimally exploit the enormous amount of oil palm frond (Kelly-Yong et al., 2007). Meanwhile, bonding strength of the BPF resin was determined by blending the resin with *Rhizophora* wood particles to produce a *Rhizophora* particleboard, which would be most beneficial in the diagnostic radiography industry (Abuarra et al., 2014). Therefore, the similar origin of resin and wood particles was chosen to investigate whether or not it would enhance the resulting bonding strength.

During this study, the expensive petroleum-based phenol usually used in conventional PF resin was substituted with phenol-rich bio-oil obtained from slow pyrolysis. It was believed that with the use of the environmentally-friendly bio-oil, BPF resin with comparable or better capability than the conventional PF resin might be produced.

MATERIALS AND METHODS

Materials

Oil palm frond was harvested in August 2014 in a plantation of Universiti Sains Malaysia (USM), Nibong Tebal, Pulau Pinang, Malaysia (5°08'48.2'N 100°29'32.0'E). Oil palm frond that was abandoned from the harvesting process was collected and the leaves attached to them were removed using a machete. *Rhizophora* hardwood was also collected in August 2014 from a charcoal factory in Kuala Sepetang, Perak, Malaysia (4°50'12.1"N 100°38'13.9"E). During the collection, bark of the *Rhizophora* was removed using a bark spud and a total of two units of bark-free hardwood were randomly chosen.

Immediately after retrieval, the oil palm fronds and the *Rhizophora* hardwood were dried in a Venticell oven at 105°C until their moisture content wasreduced to less than 10 mf wt% to avoid growth of fungus or microorganism (Abdullah et al., 2014). Then, a Hitachi band saw machine was used to cross cut the sample to an appropriate length. This was important to ensure that the samples could be milled by a Riken grinder with screen size of 1.5 mm. The properties of the two samples were later determined and are presented in Table 1. The reagents used during the synthesis of BPF resin were liquefied phenol (99%), formaldehyde (37%), sodium hydroxide (50%) and anhydrous ethanol (99%). All the reagents were of analytical or pharmaceutical grade.

Preparation of Bio-Oil: Slow Pyrolysis

In brief, slow pyrolysis of oil palm frond and *Rhizophora* hardwood was carried out in a fixed bed reactor (modified Thermolyne F62700 muffle furnace) equipped with a liquid collection system. In a typical run, approximately 200 g of biomass sample was introduced into a stainless steel pyrolyzer (diameter=7 cm, length=15 cm) and placed inside the muffle furnace. All of the related apparatus was then assembled according to the experimental setup shown in Figure 1. From the start, nitrogen gas was purged into the pyrolyser at 100 ml/min to facilitate the removal of pyrolysis vapour into the liquid collection system (Ertaş & Alma, 2010).

Table 1
Properties of oil palm frond and Rhizophora hardwood

| Properties	Oil palm frond	*Rhizophora* hardwood	Method
Structural analysis			
Cellulose (wt%)	47.34 ± 1.07	49.42 ± 0.94	D1103 (ASTM, 1978a)
Hemicellulose (wt%)	27.25 ± 1.92	26.63 ± 1.19	D1104 (ASTM, 1978b)
Lignin (wt%)	20.08 ± 2.42	18.65 ± 1.84	D1106 (ASTM, 2001a)
Extractive (wt%)	3.60 ± 0.06	1.28 ± 0.04	D1107 (ASTM, 2007)
Elemental analysis			
C (wt%)	42.91 ± 1.21	44.15 ± 1.94	
H (wt%)	6.88 ± 1.36	7.13 ± 1.05	
N (wt%)	0.47 ± 0.09	0.34 ± 0.05	Perkin Elmer Series II CHNS/O Analyzer
S (wt%)	0.03 ± 0.02	0.41 ± 0.04	
O (wt%)	46.27 ± 2.41	47.38 ± 2.10	
Proximate analysis			
Moisture content (wt%)	7.47 ± 0.25	7.61 ± 0.15	A&D MX-50 moisture analyzer
Volatile matter (wt%)	82.42 ± 1.39	84.63 ± 0.52	E872 (ASTM, 2006)
Ash (wt%)	3.44 ± 0.30	0.59 ± 0.24	D1102 (ASTM, 2001b)
Fixed carbon (wt%)	6.67 ± 1.42	7.16 ± 0.64	By difference
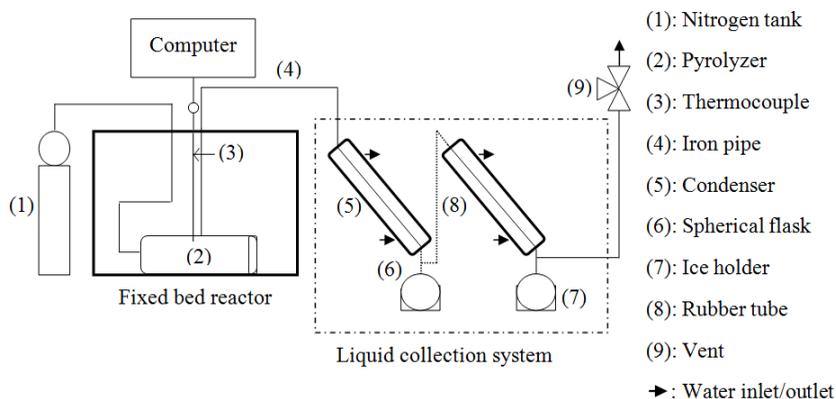
Figure 1. Experimental setup of pyrolysis

The furnace was then heated to 375°C at a steady rate of 100°C/min. These parameters correspond to the optimised yield of phenols obtained in the bio-oil (unpublished data). After one hour of holding time, the muffle furnace was turned off and allowed to stabilise to room temperature. The bio-oil, as obtained from the condensation of pyrolysis vapours, was collected, separated using dichloromethane and analysed as in Table 2 before it was used in the synthesis of BPF resin.

Table 2
Properties of Bio-oil

Properties	Oil palm frond	*Rhizophora* hardwood	Method
Element			
C (wt%)	66.23 ± 1.14	67.66 ± 1.59	
H (wt%)	9.35 ± 1.16	8.12 ± 1.44	
N (wt%)	0.05 ± 0.02	0.02 ± 0.01	Perkin Elmer Series II CHNS/O Analyzer
S (wt%)	0.00 ± 0.00	0.05 ± 0.03	
O (wt%)	23.77 ± 2.30	23.93 ± 2.58	
Ash (wt%)	0.61 ± 0.03	0.22 ± 0.06	D1102 (ASTM, 2001b)
Char (wt%)	0.32 ± 0.13	0.14 ± 0.08	Filtration method
pH	3.01 ± 0.03	2.63 ± 0.03	Accumet AB15 pH meter
Total peak area of phenols (%)	74.4	71.1	
Distribution of phenols (%)	Phenol (40.6)	Phenol (7.3)	
	Phenol, 2-methyl- (1.7)	Phenol, 2-methyl- (2.4)	
	Phenol, 3-methyl- (2.3)	Phenol, 3-methyl- (2.9)	
	Phenol, 2-methoxy- (8.5)	Phenol, 2-methoxy- (16.5)	Agilent Technologies 7890A/5975C GCMS
	4-Mercaptophenol (1.4)	Phenol, 2,4-dimethyl- (1.8)	
	Phenol, 2,5-dimethyl- (1.4)	Phenol, 2-methoxy-5-methyl- (5.8)	
	Phenol, 4-ethyl-2-methoxy- (4.4)	Phenol, 2-methoxy- (1.6)	
	Phenol, 2,6-dimethoxy- (14.2)	Phenol, 4-ethyl-2-methoxy- (3.9)	
		Phenol, 2,6-dimethoxy- (29.0)	

Synthesis of BPF Resin

The synthesis procedure was maintained in a closed system. In brief, the required volume of reagents was measured using a Fisherbrand pipette. Then, liquefied phenol, ethanol and sodium hydroxide were loaded into a three-necked flask connected to a pressure-equalising addition funnel, thermometer and cooling condenser and placed on a ceramic heating plate equipped with magnetic stirrer. Bio-oil, after the separation procedure, was also used to substitute the liquefied phenol at 25% and 75% of the total amount required. The mixture was heated to 65°C and maintained at that temperature for 30 minutes to ensure a homogenous alkaline medium was produced (Chaouch et al., 2014). After homogenisation had occurred, the temperature was raised to 80°C and formaldehyde solution was added step-wise over a period of 10 minutes. Finally, the reaction mixture was heated to 95°C and kept at that temperature for a period of time to allow condensation reaction and polymerisation to occur. After the required viscosity had seemingly been reached, the reaction was stopped and allowed to stabilise to room temperature before being dissembled. The BPF resin was then refrigerated in a sealed glass

bottle to prolong its pot life by minimising any additional slow polymerisation of phenolic rings (Sukhbaatar et al., 2009).

Characterization of BPF Resin

Several analyses such as viscosity, pH, non-volatile measurements, free formaldehyde level, pot life evaluation, DSC, TGA and bonding strength determination were conducted to study the properties of BPF resin. These properties were then compared with the properties of conventional PF resin.

Viscosity measurement was conducted using the Visco Basic Plus viscometer with L1 spindle according to D1084 (ASTM, 2016a). The pH value of the resin was determined using an Accumet AB15 pH meter. The non-volatile content of the BPF resin was evaluated at 105°C in reference to D4426 (ASTM, 2013). Free formaldehyde level was measured according to 11402 (ISO, 2012). In addition, pot life was denoted as the time taken for the initial viscosity of the resin to become twice its original, according to D1337 (ASTM, 2016b). Therefore, the viscosity of BPF resin was determined regularly, at a fixed time of interval from the first week of synthesis until the fifth week of storage.

On the other hand, DSC analysis was conducted to evaluate thermal curing properties of BPF resin using the Perkin Elmer DSC Pyris 6. Approximately 10 mg of resin was sealed in the given DSC aluminium pan, placed onto the sample holder and heated from 30°C to 250°C at 10°C/min. A flow of nitrogen gas at 20 ml/min was maintained over the sample to create a dry and reproducible atmosphere. Meanwhile, TGA was carried out to analyse thermal behaviour of the resin using the TGA/DSC-1 Mettler Toledo. The analysis started by heating the resin sample from room temperature to 700°C at a heating rate of 10°C/min. Together with the heating, nitrogen gas was purged into the system at a flow rate of 50 ml/min. To pronounce the decomposition pattern of each resin, cured conventional PF and BPF resins were used. These cured resins were obtained by heating the respective resins to their curing temperature as obtained from the DSC analysis.

Moreover, bonding strength was determined by fabricating a *Rhizophora* particleboard with 10% of the resin as binding agent. The fabrication procedure of the particleboard was conducted according to previous literature (Ngu et al., 2015). Following that, bonding strength was measured according to A5908 (JIS, 2015).

RESULTS AND DISCUSSION

Formulation

The formulation used to synthesise BPF resins was tabulated in Table 3. For easy reference, abbreviation of BPF(OP) and BPF(RS) was used denoting BPF resin originated from bio-oil of oil palm frond and bio-oil of *Rhizophora* hardwood, respectively.

Table 3
Formulation of BPF resin

Type of Resin	Bio-oil Substituted	F/P	Molar Ratio NaOH/P	EtOH/P	Time to Reach 200 cP (h)
BPF(OP25)	25	1.3	0.3	0.4	5.0
BPF(OP75)	75	1.3	0.5	0.4	3.5
BPF(RS25)	25	1.3	0.3	0.4	5.0
BPF(RS75)	75	1.3	0.5	0.4	3.5

From the preliminary study, molar ratio of formaldehyde to phenol at 1.3 was observed to produce free formaldehyde level less than the standard permissible value for formaldehyde-based resin, which was set at 0.4 wt% (Cetin & Özmen, 2002). Meanwhile, 0.3 to 0.5 molar ratio of sodium hydroxide to phenol was engaged to conform to the typical pH value of conventional PF resin, which is usually around 11 (Ayrilmis et al., 2008; Chaouch et al., 2014; Zhao et al., 2010). Different substitution levels of sodium hydroxide were initiated to counteract the different amount of acidic bio-oil within the formulation. In the case of ethanol, a lower ratio of ethanol to phenol reduced the solubility of bio-oil in the resin solution. From the preliminary study, it was observed that when the molar ratio of ethanol to phenol was less than 0.4, the BPF resin separated into two different fractions.

In general, for the same amount of bio-oil substituted during BPF resin synthesis, a similar amount of reagents and time was required to achieve the desired viscosity, regardless of the origin of the bio-oil. This was expected since the properties of the two bio-oils were comparable, as found from previous characterisation.

Meanwhile, when comparing different substitution levels of the same bio-oil, BPF resin with higher percentage of bio-oil reached the desired viscosity in a shorter time. The occurrence was most likely because a much larger and complex molecular structure existed in the bio-oil as compared to the petroleum-based phenol, increasing its degree of condensation and polymerisation (Cheng et al., 2011).

Furthermore, it was noticed that the condensation time required to achieve the desired viscosity was different in this study. Other studies reported that the condensation time taken was from 1 to 3 hours, whereas in this study, 3 to 5 hours was needed (Chaouch et al., 2014; Zhao et al., 2010). This could be explained by the inclusion of the low molar ratio of formaldehyde to phenol and the high molar ratio of ethanol to phenol during the synthesis. It is known that a low amount of formaldehyde would reduce the rate of reaction between formaldehyde and phenol, while a high amount of ethanol would slow down the condensation process as it introduced a side reaction between the ethanol and phenol (Mo et al., 2015; Yan et al., 2008). Hence, to ensure that maximum reaction and condensation occurred, a longer time was needed. Despite having an unfavourable effect on the synthesis procedure, the low amount of formaldehyde and the high amount of ethanol were still chosen to ensure that the final properties of the BPF resin were approximately similar to the conventional PF resin.

Properties of BPF Resin

The BPF resins obtained were homogenous and dark brown in color, slightly different from the reddish-brown conventional PF resins. This was probably due to the addition of dark-brown coloured bio-oil during the synthesis. The properties of the BPF resin were determined and are presented in Table 4. It was observed that all of the BPF resins successfully reached the desired viscosity of around 200 cP, as in conventional PF resin.

Table 4
Properties of resins

Type of Resin	Viscosity (cP)	pH	Non-volatile content (wt%)	Free Formaldehyde Level (wt%)
Conventional PF	250-500, 200, 233	11.75, 11.16, 10.5	47, 64, 49	Undetectable
	(Ayrilmis et al., 2008; Chaouch et al., 2014; Zhao et al., 2010)	(Ayrilmis et al., 2008; Chaouch et al., 2014; Zhao et al., 2010)	(Ayrilmis et al., 2008; Chaouch et al., 2014; Zhao et al., 2010)	(Chaouch et al., 2014)
PF	209 ± 3	9.36 ± 0.03	42.40 ± 0.11	0.00 ± NA
BPF(OP25)	220 ± 4	11.60 ± 0.03	56.96 ± 0.86	0.17 ± 0.05
BPF(OP75)	204 ± 2	11.83 ± 0.05	42.60 ± 0.41	0.41 ± 0.04
BPF(RS25)	227 ± 4	11.37 ± 0.02	59.21 ± 0.24	0.11 ± 0.02
BPF(RS75)	215 ± 2	11.60 ± 0.06	45.66 ± 0.20	0.35 ± 0.02

When comparing the origin of the resins, it was found that BPF(OP) resin had lower viscosity than BPF(RS) resin for both substitution levels. The lower viscosity of resin achieved after having similar formulation and time of condensation indicated that the BPF(OP) resin had a lower molecular weight than the BPF(RS) resin, probably due to the nature of the bio-oil (Cheng et al., 2011; Zhao et al., 2010).

It was also shown that the conventional PF resin had significantly lower pH than the other BPF resins. In most studies, it was reported that the ideal pH value for phenolic resin was between 10 and 12 (Ayrilmis et al., 2008; Chaouch et al., 2014; Zhao et al., 2010). Those with a lower pH may exhibit poor curing properties as polymerisation and curing of phenolic resin accelerated at a very alkaline pH. However, due to the complicated mechanism of the alkaline catalyst, the explanation behind the occurrence was reported as unclear (Pizzi, 1994). In this study, the formulation was prepared according to the typical pH value of conventional PF resin instead of the purchased conventional PF resin, hoping that with a higher pH, the curing properties of the BPF resin would improve.

In addition, for the similar amount of bio-oil substituted, BPF(OP) resin had a higher pH than did the BPF(RS) resin, even though a similar amount of sodium hydroxide was added. This finding was in accordance with the pH value of the respective bio-oil.

Furthermore, it was noticed that all of the BPF resins had higher non-volatile content than the conventional PF resin. The high amount of non-volatile content is favourable as it reduces the required amount of resin to be added during the production of panels; hence, decreasing the consumption of the formaldehyde-based resin makes it more economical and user-friendly.

Non-volatile content of phenolic resin is closely dependent on the volatile components such as free phenol and free formaldehyde. High amount of volatile components in the resin causes low value of non-volatile content as in the case of conventional PF resin. It was observed that the conventional PF resin had low free formaldehyde level, which raised the possibility that it might use a low level of formaldehyde. It is worthy to note that the addition of a low level of formaldehyde caused an imbalance reaction between the phenol and formaldehyde, leaving excess unreacted phenol at the end of the synthesis procedure. Upon heating, this free phenol vapourised from the resin and as phenol has a higher molecular weight than formaldehyde, the vaporisation of free phenol from the resin caused a more significant reduction in terms of non-volatile content than the vaporisation of formaldehyde.

On the other hand, when comparing a different substitution level of the same bio-oil, those with a higher substitution level had a lower value of non-volatile content. The most possible explanation was that together with the increase of bio-oil, the amount of unreacted free formaldehyde might have increased as well. Therefore, when this type of resin was heated, a large amount of volatile was evaporated and finally, the non-volatile content was reduced significantly. Similarly, when comparing the origin of the resins, BPF(OP) resin had lower non-volatile content. Hence, it was expected that this type of resin had a higher amount of free formaldehyde than the BPF(RS) resin.

From Table 4, it was found that all the resins exhibited free formaldehyde levels around 0.4 wt%. As for the purchased conventional PF resin, the free formaldehyde level was reported as being not detectable, cited from the Safety Data Sheet (SDS) provided by the supplier. Meanwhile, for all other BPF resins, the free formaldehyde level was observed to increase with an increase of the substitution level of phenol with bio-oil. This was mostly due to the lower reactivity of bio-oil over phenol or the lower number of active sites especially in –*otho* and –*para* position to the phenolic hydroxyl group of the bio-oil that might cause poor interaction between phenol and formaldehyde, leaving an amount of free formaldehyde at the end of the synthesis. When comparing the origin of the BPF resins, it was found that BPF(OP) resin had a higher free formaldehyde level than BPF(RS) resin, which suggested lower reactivity of bio-oil produced from oil palm frond than the one produced from *Rhizophora* hardwood, possibly due to lesser active sites in the phenolic rings (Chaouch et al., 2014; Cheng et al., 2011).

Pot life of the BPF resin was also investigated by constantly measuring of the viscosity for five consecutive weeks, as shown in Figure 2. In the earlier weeks, the viscosity increased at a slower rate. However, since resole-type phenolic resin is capable of curing without any addition of heat or curing agent, slow polymerisation occurred during storage time. The polymerisation process is an exothermic reaction due to the formation of new polymer chains that enhance the release of heat energy. This heat energy catalyses the rate of polymerization, causing an exponential increase in viscosity over time.
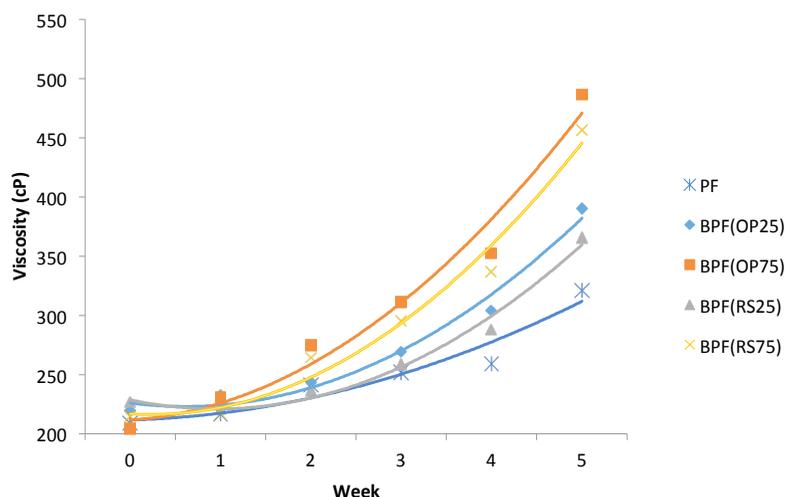
Figure 2. Pot life of resins

From Figure 2, it was seen that conventional PF resin had the greatest stability over time, with only 35% of increase from the initial. Since it had a lower pH value than the other BPF resins, its rate of polymerisation is lower, improving its stability over time. It was also observed that the viscosity of BPF resin with 25% substitution level increased at a slower rate compared to those with a 75% substitution level, with a total change of 38-44% and 53-58%, respectively. As previously characterised, the added bio-oil had a small amount of ash/char that affected the stability of bio-oil negatively (Pollard et al., 2012). Therefore, a higher substitution level of bio-oil in place of phenol increased the amount of ash/char in the BPF resin, which consequently reduced its stability compared to those with a lower substitution level. Similarly, the more pronounced increase in the viscosity of BPF(OP) resin than in that of BPF(RS) resin can be explained by the higher amount of ash/char content in the corresponding bio-oil.

Although the pot life of resins was observed to be around the fifth week (the week at which the viscosity of the resin doubled), it was important to note that with proper storage in a low temperature environment, the pot life can be prolonged.

Thermal curing properties of the resins were analysed using DSC results. In an attempt to enhance the exothermic peak of each resin, the DSC curves were plotted from 100°C to 230°C, shown in Figure 3. The temperature at which curing reaction occurred was represented by this exothermic peak. During curing reaction, further condensation and polymerisation occurred to produce a more stable cross-linked resin structure. Curing patterns obtained for all resins were found to be consistent with those typically observed for conventional PF resin, with a single exothermic peak only (Mo et al., 2015).
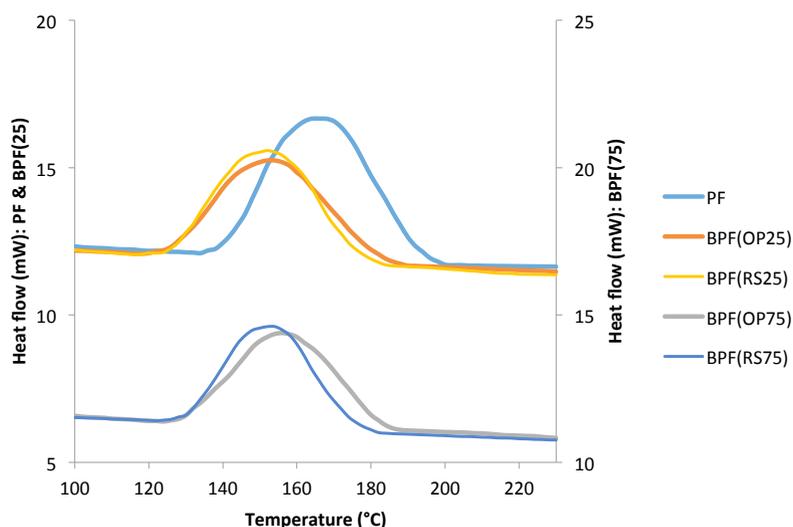
Figure 3. DSC of resins

However, it has been previously reported that the exothermic peak temperature of conventional PF resin was usually at 150°C (Cheng et al., 2011; Zhao et al., 2010). In this study, it was observed that the conventional PF resin had a higher exothermic peak temperature, with a value of 166°C. Since the detailed composition of the conventional PF resin used in this study and other studies was not known, it was difficult to speculate on the mechanism associated with the behaviour of both. However, the high peak temperature of the conventional PF resin used in this study might be attributed to its low pH value, causing it to less likely favour the condensation reaction and, therefore, require higher heat energy to allow complete condensation and polymerisation.

Interestingly, the curing temperature of BPF resins obtained was lower than that of the conventional PF resin used in this study and comparable with the conventional PF resin used in the other studies. The peak temperature of BPF(OP25), BPF(OP75), BPF(RS25) and BPF(RS75) resins were obtained at 154°C, 156°C, 152°C and 154°C, respectively. The occurrence was probably due to the enhanced alkaline environment of the BPF resins, which in turn helped to promote condensation and accelerate curing reaction (Pizzi, 1994).

One previous study suggested that the presence of bio-oil actually improved curing properties. A small amount of bio-oil was believed to favour thermal curing reaction governed by phenol, while a high amount of bio-oil would retard the thermal curing reaction due to the low reactivity of bio-oil (Cheng et al., 2011). In this study, the curing reaction between the BPF resins indeed supported the previous deduction.

In addition, the thermal stability of cured PF and BPF resins was evaluated according to the TG analysis. The result showed that all of the resins had an approximately similar thermal decomposition pattern. It has been previously reported that the decomposition of phenolic resins occurred in three major events known as post-curing, thermal decomposition and ring stripping (Cheng et al., 2011). Post-curing reaction, which could be attributed to further cross-linking and polymerisation reactions, usually occurs when cured resin is subjected to elevated

temperature. The purpose of post-curing reaction is to improve the mechanical properties of resin. However, during this post-curing reaction, low molecular weight compounds such as unreacted phenol or formaldehyde and short-chain polymers tend to vapourise (Ko & Ma, 1998). Meanwhile, thermal decomposition of resin could have been ascribed due to the breakdown of the previously formed methylene bridges linkage into aldehydes and phenols (Papadopoulou & Chrissafis, 2011, Chaouch et al., 2014). Ring stripping was associated with the breakdown of the phenolic ring network (Chaouch et al., 2014). All of these events consequently contribute to the weight loss of resin during TG analysis.

From Figure 4.16, it was observed that the first thermal event occurred from 50°C to 250°C with a total weight loss of 11% for conventional PF resin and 17% to 20% for BPF resins. The second thermal event was obtained from 250°C to 500°C with a total weight loss of around 10% for conventional PF, BPF(OP25) and BPF(RS25) resins. BPF(OP75) and BPF(RS75) resins experienced a significantly higher percentage of weight loss at 23% and 24%, respectively. The third thermal event was observed to occur within 500°C to 700°C with a comparable percentage of weight loss. Both conventional PF and BPF resins showed total weight loss between 9% and 12%.
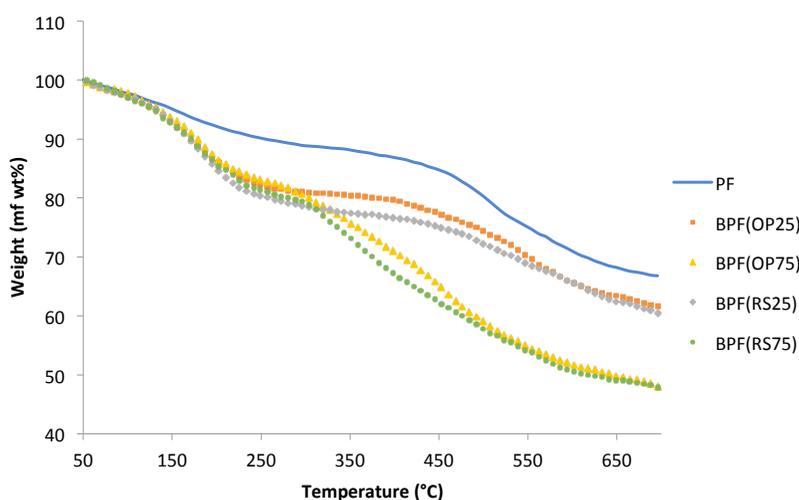

Figure 4. TGA of resins

It can be concluded that thermal stability of PF resin was superior to any other BPF resins, with the lowest percentage of weight loss happening in all three thermal events and the highest amount of final weight residue. In the case of BPF resin, it was seen that when a higher substitution level of bio-oil was incorporated, more pronounced weight loss occurred throughout the heating, resulting in lower weight residue. The occurrence was probably due to the addition of the less reactive and complex bio-oil to the synthesis of resin, causing an increase in the formation of any side chain present within the bio-oil molecules, such as the Tollens reaction, where the lignin side chains are substituted by aliphatic methylol groups

(Kalia & Avérous, 2016). This undesired side chain was easily decomposed with an increased temperature. Furthermore, the presence of an undesired chain might result in a rather weak cross-linked network of polymers and, therefore, affect thermal stability negatively (Cheng et al., 2011, Chaouch et al., 2014).

From Table 5, it was noticed that when different types of resin were used, no significant change to bonding strength was observed, except for a slight increase or decrease in accordance to the viscosity of resin. In cases of resin with lower viscosity such as PF resin and BPF resin with 75% substitution level, the ability of the resin to readily flow and spread itself within the particleboard increased. When this occurred, the distribution of the resin across the particleboard improved, causing more interaction between the resin and *Rhizophora* wood particles. During particleboard formation, the distributed resin cured to a stable polymer and became chemically attached to the wood particles, giving the particleboard higher bonding strength (Pizzi, 1994).

Table 5
Bonding strength of particleboard bonded with phenolic resins

Type of Resin	Bonding Strength (MPa)
PF	1.61 ± 0.13
BPF(OP25)	1.46 ± 0.03
BPF(OP75)	1.65 ± 0.10
BPF(RS25)	1.37 ± 0.13
BPF(RS75)	1.51 ± 0.02

CONCLUSION

The bio-oil produced from slow pyrolysis of oil palm frond and *Rhizophora* hardwood was successfully used to partially substitute petroleum-based phenol in the formulation of resole-type BPF resin. In this study, all of the synthesised resins were seen to successfully imitate the properties of conventional PF resin. These BPF resins were more than capable of reaching the typical viscosity and pH value of conventional PF resin. The BPF resins also had an improved value of non-volatile and better curing properties than the conventional PF resin. Bonding strength of particleboard bonded with the BPF resins was also found to be comparable with those bonded with conventional PF resin. The only downsides to these BPF resins were the increase in free formaldehyde level and the reduction of their thermal stability. These outcomes were produced probably due to the addition of less reactive bio-oil, preventing maximum interaction between phenol and formaldehyde during the synthesis procedure as well as inducing various undesired side reactions that would easily decompose in high temperature.

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