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Yeoh Beng Hoong, Antonio Pizzi, Luqman Abd. Chuah, Jalaluddin Harun

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Phenol-Urea-Formaldehyde Resin Co-Polymer Synthesis and Its Influence on Elaeis Palm Trunk Plywood Mechanical Performance Evaluated by ^{13}C-NMR and MALDI-TOF Mass Spectrometry

Yeoh Beng Hoong [a,c]*, Antonio Pizzi [b], Luqman Abd. Chuah [c], Jalaluddin Harun [a]

[a] Fibre and Biocomposite Centre, Malaysian Timber Industry Board (MTIB), Lot 152, Jalan 4, Kompleks Perabot Olak Lempit, 42700, Banting, Selangor, Malaysia.

[b] ENSTIB-LERMAB, University of Lorraine, 27 rue Philippe Seguin, BP 1041 88051, Epinal, France.

[c] Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia.

*Corresponding author. Tel: + 60 12 4565631; Fax: + 60 3149 1607

E-mail address: frence_yeoh@yahoo.com / yeoh@mtib.gov.my (Y. B. Hoong)

Abstract

This study evaluated a new method of producing phenol-urea-formaldehyde (PUF) adhesives formulated differently under actual “in-situ” resin synthesis conditions. This was carried out by co-polymerizing urea formaldehyde (UF) resin with phenol-formaldehyde resin in the core layer of low molecular weight (LMW) phenol-formaldehyde (PF) resin treated Elaeis palm trunk veneers during the gluing process of Elaeis palm plywood. Matrix assisted laser desorption Ionization time of flight (MALDI-TOF) mass spectrometry (MS) illustrated and confirmed a series number of the phenol-urea co-condensates repeating unit in the prepared PUF resins which corroborated well with its mechanical properties (modulus of elasticity and modulus of rupture), bonding quality (dry test and weather boil proof or WBP test) and physical properties. A series of PF, UF and PUF resins oligomers forming repeating units up to 1833 Da were identified. Besides that, the solid state ^{13}Carbon nuclear magnetic resonance (NMR) interpretation identified that the signal at 44-45 ppm and 54-55 ppm corresponding to methylene bridges were co-condensated in between phenol and urea in the PUF resin system. The ^{13}C NMR investigation showed that the synthesis process of PUF resin contained no free formaldehyde elements. Furthermore, the proportion of urea and methylolureas in the mixture to synthesis PUF resin were sufficient and incorporated well into the formulation by reacting with LMWPF units to form co-condensed methylene bridges. This study showed a new and useful method to synthesize PUF resin during the gluing process of manufactured Elaeis palm plywood which can also enhance the performance of Elaeis palm plywood panels for structural instead of utility grade applications.

Keywords : A. Phenol-urea-formaldehyde; Resin; 13C NMR; MALDI-TOF; Mechanical; Bonding

1.0 Introduction

Phenol-formaldehyde (PF) can be classified into novolak (acid cure and excess of phenol) and resol type (alkaline cure and formaldehyde in excess) resins and have been widely used as a synthetic base adhesive in the wood base-industry for many centuries [1]. PF resins dominate the market for the manufacture of exterior type wood composites such as plywood, fibreboard, laminated veneer lumber (LVL), oriented strawboard (OSB) and particleboard. In fact, the main reasons PF resin is extensively used in the wood manufacturing industry are its resistance to water, weather resistance, good bonding properties as well as the minimal health problem of formaldehyde emission from the end products [2]. Over the past decade, research and development work on resins with different formulations to achieve specific requirements in the wood-composite industry and market have been rigorous. To date, many excellent formulations have been introduced to the market. Although some industry work remains in a premature stage, nonetheless the knowledge on the “know-how” have been implemented in areas of developing and improving the resins performance.

Resin treatments of wood and non-wood materials with low molecular weight (LMW) phenolic resin to enhance the physical, mechanical, and flame resistance of panel products have been extensively reported and studied [3-8]. An advantage of low molecular weight resins are their relatively, short chain, smaller molecules which can easily penetrate into wood cells thus improving mechanical properties. A method of improving the mechanical properties of non-wood materials by treatment with LMWPF resin has also been reported [9-14]. The main drawback of treatment with LMWPF resin is a much longer pressing time. Corresponding to Hoong et al. [15-18], LMWPF resin contains a high number of methylol groups in the main polymer chain compared to commercial PF resin, thus a longer time is required to cure the resin. A method of adding urea into the PF resin system to form phenol-urea-formaldehyde (PUF) has been studied and reported where this method improved the curing behavior and mechanical strength properties of wood-based products used in exterior-grade applications [6, 8, 19]. However, excessive amounts of urea-formaldehyde (UF) applied also reduced its waterproof performance [20]. Pizzi [21] reported that urea is incapable of condensing to UF resins in a fairly alkaline environment but its reaction with formaldehyde to form methylol urea is faster under alkaline conditions. The same is valid with any source or type of formaldehyde; including the methylol group of PF resin (It is not valid for the methylol group of UF resins as an inverse reaction occurs where depolymerisation happens at alkaline pH).

Based on our previous research, pre-treatment of Elaeis palm veneer with LMWPF resin successfully improved the quality of plywood [22-26]. However, production cost and effective pressing times are highly important in Elaeis palm plywood manufacture, thus, limiting the amount of LMWPF resin used or partially replacing it with cheaper resin may cause a significant reduction in cost. The aim of this study was to investigate the effectiveness of an experimental method of introducing UF into the synthesis system with adequate co-reaction to form a PUF resin system during the manufacturing process. The effect of the resin-structure distributions on mechanical and bonding quality of the resins were investigated by matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry (MS) and solid state ^{13}Carbon nuclear magnetic resonance (NMR).

2.0 Experiments

2.1. Material preparation

Elaeis palm veneer peeled from matured Elaeis palm trunk (around 25 years) with 4.5 mm thickness were used as the raw material. The veneers were peeled into sizes of 920 x 1220 mm and then air-dried to a moisture content (MC) of 10-15 %. Only veneers from the middle and outer parts of the trunk were used.

2.2. Preparation of LMWPF and UF resin

LMWPF resin was obtained from Malayan Adhesive and Chemical (M) Sdn. Bhd. LMWPF resin (approximately 500-600 MW [27]) with 32 % solid content used as a filling agent in the pre-treatment of Elaeis palm veneers were prepared according to a method by Hoong et al. [24-26] by reacting phenol and formaldehyde in alkaline conditions. This resin cooking procedure followed by normal PF resin cooking for plywood with modification of the methylolation step duration was maintained for less than 4 hr. The properties of the resin were 45 % solid content, 1.24 specific gravity, 0.91 poise and pH 10.4.

The UF resin was produced to obtain resin with typical properties of pH 7.5-8.5, 42 % solid content, specific gravity of 1.19, viscosity ranging from 1.5 - 2.0 poise, and pot life of 35 - 55 min. The resin was produced using a typical UF cooking procedure. The mixture was heated ~~up~~ and then reacted under alkaline condition using sodium hydroxide to start the methylolation process. The resin was then adjusted to an acidic environment ~~and underwent~~ followed by condensation at a pH ranging from 4-6 at various temperatures (80-90 °C) to obtain target end-point viscosity within the time limit of 90-120 min. The reaction at this stage was terminated by adjusting the mixture to a target pH of 7.5-8.5. The resin was then cooled to below 40 °C to ensure resin preservation.

2.3. Veneer enhancement

In the pretreatment stage, dried veneers were soaked in LMWPF with 30 % solid content for 10 sec. After soaking, the veneers were then roller-pressed (30 bars) to ensure an adequate penetration of the resin into the veneers. After that, the veneers were stacked for further drying at 70 °C in an industrial oven to achieve a targeted final MC of below 20 %.

2.4. Production of plywood panels

In the plywood manufacturing stage, 3-plies of treated dried veneers with sizes of 1220 x 2440 mm were produced from a total of 6 pieces of short core veneers (920 x 1220 mm) with 1 long core veneer (1220 x 2440 mm). The pre-treated Elaeis palm veneers were then laid-up as a cross laminate and hot pressed at 140 °C. No additional glue was used in this step as residual LMWPF resin from the pre-treatment stage was sufficient for this purpose.

Another batch of 3-ply treated Elaeis palm veneers were sent to a roller resin spreader for the gluing process. Only the core layers were glued with commercially available UF resin which was mixed with industrial wheat flour and hardener (ammonium chloride). The adhesive mixture was spread on the veneers at 250 g/m^2 spread rate (single glue line). The assembled veneers were then cold pressed for 10 min and hot pressed at 140 °C for 16 min. The plywood panels were then conditioned in a conditioning room maintained at a relative humidity of 65 % and a temperature of 20 °C for 5-7 days prior to the evaluation of their properties.

2.5. Physical property testing on Elaeis palm plywood

The density of plywood was determined in accordance with European standard EN 323: 1993 [28] by measuring the mass and volume of each sample. Ten samples of each treatment were weighed using an analytical balance. The density was calculated using the following equation:

$$\text{Density, g/cm3} = \frac{\text{Mass}}{\text{Volume}} \tag{1}$$

2.6. Mechanical properties and bonding integrity testing on Elaeis palm plywood

2.6.1. Static bending test

Static bending tests were carried out according to the European Norm EN 310:1993 [29]. A total of 50 specimens measuring 290 mm x 50 mm x 12 mm were prepared. These samples were tested using the Shidmazu-15 Universal Testing Machine with 50 kN capacity employed as bending strength. Statistical analyses were carried out to determine the effect of treatment, veneer type and adhesive spread amount on the bending (i.e. modulus of rupture, MOR) and stiffness (i.e. modulus of elasticity, MOE) of the plywood panel.

2.6.2. Bonding quality assessment of panel

Adhesive bonding properties were evaluated according to European norms EN 314-1[30] and EN 314-2: 1993 [31], respectively. All shear test plywood specimens were tested in dry (interior type bond) and WBP (exterior type bond) testing conditions. For boiling test: specimens were soaked in boiling water under normal atmospheric conditions for 72 hr followed by cooling of specimens in water (20 + 3) °C for 1 hr.

2.7. Solid state ^{13}C NMR analysis

Both PF and PUF resins were cured in a laboratory oven and ground into fine powder and analysed using solid state CP-MAS ^{13}C NMR analysis. The spectrum was recorded at room temperature under CP-MAS (cross polarization magic angle spinning) on a Bruker AV400 solid state NMR with a spectrometer frequency of 62. 90 MHz. The contact plus was 1000 µsec and the number of scans was 1000. All spectra were run with a relaxation recycle delay of 5 sec and chemical shifts were accurate to 1 ppm.

2.8. MALDI – TOF a mass spectrometry measurement

The spectra were recorded on a KRATOS Kompact with a MALDI 4 instrument. The irradiation source was a pulsed nitrogen laser. The wavelength of one laser pulse was 337 nm applied for 3 ns. The experimental condition used was: mass- high (20 kV acceleration voltage), polarity – positive, fight path- linear 100-150 pulse per spectrum and 200-800 ns time of delayed extraction technique.

2.9. MALDI – TOF mass spectrometry preparation

The PUF resin (4 mg) was dissolved in 1 ml acetone. The solution was then mixed with an acetone solution (10 mg/mL acetone) of the matrix. 2, 5-Dihydroxy benzoic acid was used as the matrix and NaCl (4 mg/mL) was mixed with the matrix to enhance ion formation. The sample solution and the matrix were mixed accurately and 0.5 – 1 µl of mixture was placed on the MALDI target. After the solvent was evaporated, the MALDI target was deposited into the spectrometer.

3.0 Result and Discussion

3.1 Properties of the Elaeis palm plywood.

The physical properties, mechanical properties and bonding shear strength of commercial and treated Elaeis palm plywood panels at different resin conditions are presented in Table 1. As can be seen from Table 1, the mechanical properties (MOE and MOR) and bonding shear strength (under dry and WBP test conditions) for all treated Elaeis palm plywood panels were significantly higher compared to the commercial Elaeis palm plywood (control). The results indicate that the MOR and MOE of the Elaeis palm plywood panels increased with resin treatment. The MOR and MOE values of treated Elaeis palm plywood panels where higher than the control Elaeis palm panels. The mechanical properties for the Elaeis palm panels which were made via pre-treatment with LMWPF + UF resin had the highest values with an improvement of 97 % in MOR and 43 % in MOE compared to the commercial Elaeis palm plywood and an improvement of 13.5 % in MOR and 8.0 % in MOE compared to the plywood treated with LMWPF resin only.

The average bonding shear strength showed a similar trend to the MOE and MOR results where all treated Elaeis palm plywood had higher values compared to the commercial Elaeis palm plywood panels. The average dry shear test results were 1.10 MPa, 1.20 MPa and 1.57 MPa for control, LMWPF treated and LMWPF + UF treated, respectively while WBP shear tests yielded the following results; 0.56 MPa, 1.02 MPa and 1.32 MPa for control, LMWPF treated and LMWPF + UF treated, respectively. Results for dry and WBP tests for all treated

Elaeis palm panels achieved the minimum requirement set by EN 314-2 [14], plywood bond quality for the bond quality of veneer plywood for interior use and outdoor applications.

Detailed explanations of the advantages and effectiveness of the resin treatment method to enhance the properties (physical, mechanical and bonding) of Elaeis palm plywood were discussed in previous publications [23-26]. However, an interesting finding was observed in this study where the performance of treated Elaeis palm plywood improved significantly especially for the bonding shear and mechanical properties. This might be due to the well co-condensed LMWPF and UF resin at the glue line during the gluing process. However, a previous study by Lee and Kim [32] showed, from NMR analysis, that there was no significant co-condensation between urea and phenolic units with the different urea addition methods during the synthesis of PUF resin. Therefore, further fundamental investigation was carried out to study the resin bonding properties using solid state ^{13}C NMR and MALDI-TOF-MS.

3.2 Solid state ^{13}C NMR analysis of PUF resin

The chemical structure of synthesized PUF resin copolymers was illustrated by ^{13}C NMR. The chemical shifts assignments of carbons in LMWPF and PUF prepolymer is summarized in Table 2 according to published literature [4,7,8,33-35] to assist in the interpretation and identification of peaks in regions from 20 to 200 ppm.

The solid state ^{13}C NMR spectra of PF resins and PUF resin are shown in Fig. 1 and Fig. 2. An interesting feature can be observed from the ^{13}C NMR spectrum where both UF and LMWPF resin co-polymers used to form PUF must have formed via methylene bridges between phenol and urea in the analysis sample. As can been seen in Fig. 2, these linkages are present between urea and phenol and can be detected in peak regions of 40-42 ppm and this finding is confirmed by Schmidt et al.[36]. There are several published reports demonstrating that co-condensation process between phenolic components and urea components might or might not occur in the synthesis of PUF resin. A study by Zhao et al. [19] illustrated and determined the identified signals appearing from a PF resin co-reacted under alkaline condition with urea on phenol copolymerized to yield PUF were found through liquid phase ^{13}C NMR chemical shifts. While, Fan et al. [7] also investigated the cure-acceleration effects of catalysts on the chemical structure and characteristics of a PUF resin via ^{13}C NMR. It was noted that weak chemical shifts were found in the ^{13}C NMR spectra at 44.0 ppm, 48.0 ppm, 55.0 ppm, 68.0 ppm, and 71.8 ppm. These peaks were not found when compared with the ^{13}C NMR spectrum of the current PF resin (Fig. 1) which clearly indicated that the methylene bridges were formed in between phenolic rings and urea components. Based on the assigned signals from published literature, these chemical shifts for the PUF (Fig. 2) indicate that a co-condensation reaction was clearly present $^{\text{which}}$ is confirmed by a published research report [19]. Another interesting finding was observed whereby no peak occurred in the region of 162-164 ppm, where the peaks were attributed to the carbonyl group of free urea. Indeed, this provides very useful information for UF resin in which urea was fully reacted and the amount of urea applied into the UF resin system was sufficient in the synthesis process of PUF resin.

Based on the study, 2 chemical shifts (33.3 ppm and 39.8 ppm) were indentified and present in the region of 29.0 – 42.0 ppm for both LMWPF resin and PUF resin. The chemical shift around this region showed that the co-condensation of phenol methylol was present in the system during the pre-drying or pre-curing stage of the treated Elaeis palm veneers with LMWPF resins under 70°C. The chemical shift at 151.2 ppm is assigned as carbon (C1) alkylated at two ortho (2, 4) positions, or 2, 4, 6 positions which was higher than the chemical shift of the ortho alkylated group at 153.1 ppm and greater than the para alkylated group between 154.2 ppm and 156.4 ppm. The chemical shift at 159.5 ppm was assigned to monosubstituted urea including monomethylolurea and mono-hydroxybenzyl urea [7,19]. This chemical shift was also attributed to poly-substituted urea including di- and trimethylolureas, and bis, tris (hydroxybenzyl) ureas [7,37].

The chemical shift at 71.8 ppm is attributed to linear methylene ether bridges between urea components, notwithstanding that the addition of methylol groups might reduce the resins ability to resist water. In fact, the addition of methylol groups might enhance the elasticity of the cured resin and improve shrinkage properties [38, 39]. The chemical shift in the region 171.0-172.0 ppm in the LMWPF resin is assigned to the carbon of formic acid, the formation of which might be caused by the oxidation of formaldehyde [40]. However, no chemical shift was observed for PUF resin in Fig. 2.

No signal was observed in the region of 80-90 ppm which is attributed to free formaldehyde in the spectrum of PUF [33]. This finding proved that the mechanism of cross linking among the three components (low molecular weight phenol, urea, formaldehyde) by the addition of UF into the copolymer LMWPF resin during the glue spreading process was fully reacted in comparison to other processes of synthesis [39]. A similar study reported that low condensation PF resins co-reacted under alkaline conditions with up to 42% molar urea on phenol during resin preparation were found to yield PUF resins capable of faster hardening times than equivalent pure PF resins prepared under identical conditions [19]. Once heat is introduced, a shorter hot pressing time might be sufficient to cure the resin and a low gas formaldehyde emission Elaeis palm plywood panel is expected to be obtained, because the ^{13}C NMR results indicated there is no formaldehyde gas emitted and excessive urea in the resin system. Therefore, it can be shown that a reduction in the hot pressing time from 18 min to 16 min can be achieved without harming the total performance of the treated Elaeis palm plywood panel as indicated in Table 1.

3.3 MALDI- TOF spectra analysis of PUF resin

MALDI-TOF techniques have been employed in the analysis of oligomers prepared from natural polyflavanoid [41] and other polycondensation resins [36,42]. The main advantage of the MALDI-TOF technique is that it is capable of providing a complete mass range for a small amount of analyte. This technique has been widely used to determine large and complex series of oligomers or molecular level materials for wood adhesives (UF, PF, MUF) and other polycondensation resins, in which information provided by ^{13}C NMR is limited. The oligomer fragment distribution of synthesised PUF resin, which has been formulated by addition of UF resin in the semi-cured LMWPF resin, is shown in Table 3.

The MALDI-TOF mass spectra showed clear repetitive patterns of peaks that allow for the identification of specific oligomer series present in the PUF resin. The MALDI spectra also showed that PUF resin oligomers prevalently contained repeating units of 72 Da and 106 Da. The results in Table 2 show that PUF resin oligomers consist of pure PF units, pure UF units and mixed PUF units. The calculation of the expected oligomer resin distribution are based on the molecular weight at the main repeating unit at 72 Da for UF fragments (A unit) and 106 for PF fragments (B unit) in Fig. 3 and Fig. 4.

The MALDI-TOF spectrum in Fig. 5 and Table 3 of oligomer distribution showed that co-condensation occurred and cross-linking was present during the LMWPF oligomers reaction with UF oligomers. A clear and noticeable proportion of methylene-linked phenol to urea co-condensation was detected in the PUF resins spectrum, also by connecting phenol to phenol and urea to urea. The MALDI-TOF spectra clearly confirmed that the mixing of UF and PF resins occurred by cocondensation when heat was introduced to the assembled plywood during the hot-pressing stage. For example, the peak at 178 Da for Phenol-CH_2-Urea-CH_2 is attributed to the 1 repeating unit of 106 Da (B unit) and 72 Da (A unit). Further addition of units of UF and PF fragments can obtain the peak of 364 Da or Phenol-CH_2-Urea-CH_2-Phenol-CH_2-Urea with Na+. An addition of repeating units of UF and PF fragments at this peak resulted in the peak at 539 Da. A very interesting pattern of a series of “block polymer” is illustrated from the MALDI-TOF spectrum in Fig. 5. Another interesting interpretation from the MALDI-TOF spectra at peaks 1213 Da, 1375 Da, 1551 Da, 1712 Da to 1888 Da indicated the end of co-codensation between phenol and urea through methylene bridges. The PUF oligomers at 1213 Da were formed by the addition of Phenol-CH_2-Urea-CH_2 repeating units into the oligomer chain at 1037 Da. Consequently, the addition of CH_2-Urea-CH_2-Urea-CH_2OH into 1213 Da repeating units formed longer PUF oligomers at 1375 Da. The added repeating units are attached to phenol or urea in the body of the main skeleton, as shown in Fig. 6. Consequently, Fig. 7 shows the start of branching with the addition of either 175 Da (-Phenol-CH_2-Urea-) or 160 Da (-CH_2-Urea-CH_2-Urea-CH_2OH-) in phenol or urea. A similar finding supports the MALDI-TOF spectra result in that hydroxymethyl groups can be situated either on the urea or on the aromatic nuclei of the phenol [35].

4.0 Conclusion

Based on the findings of this study, the resin treatment method applied in Elaeis palm plywood manufacture showed significant improvements in the quality of the end product and also proved that the applied method tended to enhance cross-linking mechanisms between the two different resin systems; LMWPF resin and UF resin co-polymerized to form PUF resin without harming resin properties. The MALDI-TOF MS spectra identified several series of repeating units of PUF resin and phenol-urea co-condensates in the resin system. The proportion of methylene bridges linking phenol to urea were identified in the form of methylene bridges linking phenol to phenol and urea to urea. In addition, solid state ^{13}C NMR investigations confirmed that (1) methylene bridges did occur at signal 44 ppm; (2) the unsubstituted urea signal at 162-164 ppm are not presented; (3) unbonded formaldehyde signals were not found at 172 ppm and (4) the peak at 54-55 ppm is attributed to co-condensation of PUF resin where the phenolic and urea nuclei were substituted.

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Figure captions

Fig. 1.

Solid state ^{13}C NMR spectrum of the LMWPF resin.

Fig. 2.

Solid state ^{13}C NMR spectrum of the phenol-urea-formaldehyde cocodensation resin.

Fig. 3.

Repeating unit of urea-formaldehyde

Fig. 4.

Repeating unit of phenol-formaldehyde

Fig. 5.

The MALDI-TOF fragment spectrum of the phenol-urea-formaldehyde resin.

Fig. 6.

A proposed oligomer structure of phenol-urea-formaldehyde repeating unit.

Fig. 7.

A propose branching structure “block polymer” of urea-formaldehyde attached on the phenol main skeleton.

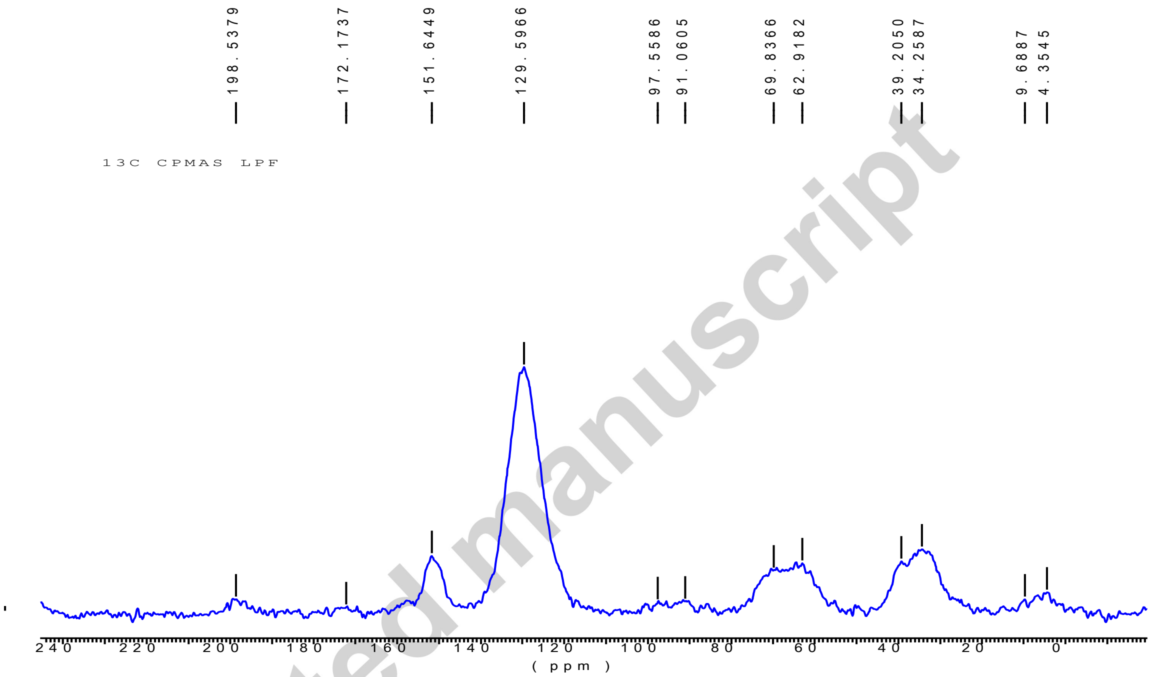

Fig. 1. Solid state ^{13}C NMR spectrum of the LMWPF resin.

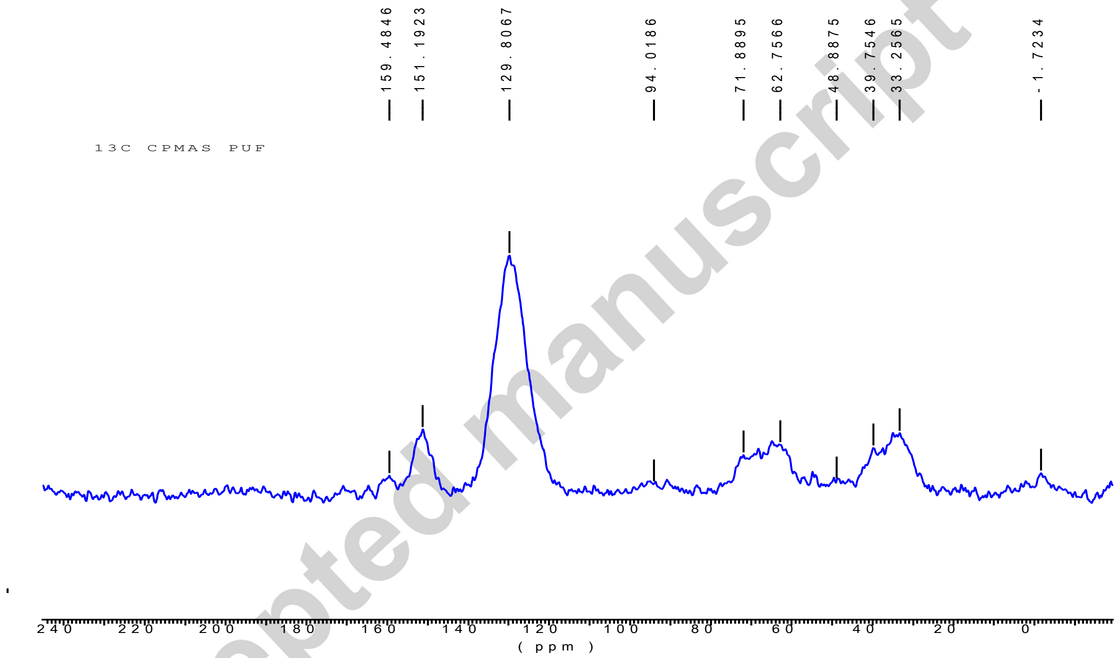

Fig. 2. Solid state ^{13}C NMR spectrum of the phenol-urea-formaldehyde cocodensation resin.

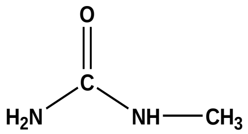

Fig. 3 Repeating unit of urea-formaldehyde

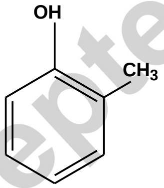

Fig. 4 Repeating unit of phenol-formaldehyde

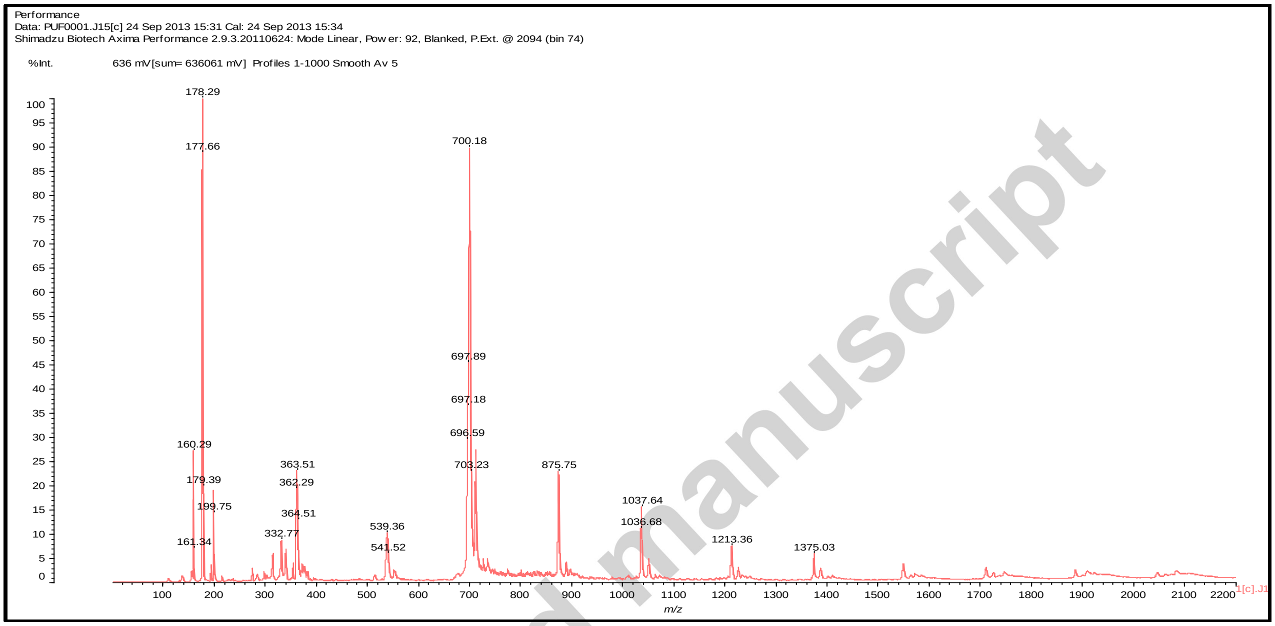

Fig. 5. The MALDI-TOF fragment spectrum of the phenol-urea-formaldehyde resin.

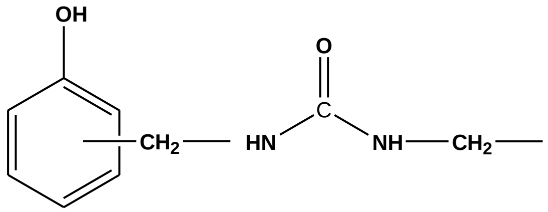

Fig. 6. A proposed oligomer structure of phenol-urea-formaldehyde repeating unit.

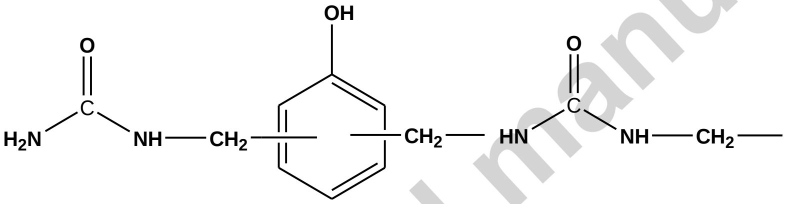

Fig. 7. A proposed branching structure “block polymer” of urea-formaldehyde attached on the phenol main skeleton.

Table captions

Table 1

The mechanical properties, physical properties and bonding quality of Elaeis palm plywood treated with different resins formulation.

Table 2

Solid state ^{13}C NMR chemical shift for phenol-urea-formaldehyde prepolymer resin [4,7,8,33-35].

Table 3

Distribution fragment of phenol-urea-formaldehyde resin oligomers by MALDI-TOF analysis.

Table 1: The mechanical properties, physical properties and bonding quality of Elaeis palm plywood treated with different resins.

Plywood	Mechanical Properties		Physical Properties	Bonding Integrity				Press time
	MOR (MPa)	MOE (MPa)	Density (g/cm^3)	Dry Shear (MPa)	Wood failure (%)	Wet Shear (MPa)	Wood failure (%)	min
Elaeis palm (control)	30.7 (4.8)	4370 (330)	540 (47)	1.10 (0.3)	100	0.56 (0.32)	100	11

LMWPF treated	53.3 (4.1)	5855 (378)	630 (38)	1.20 (0.14)	20	1.02 (0.11)	20	18
UF + LMWPF Treated	60.5 (3.6)	6349 (273)	779 (43)	1.57 (0.11)	60	1.31 (0.15)	80	16

Table 2 : Solid state ^{13}C NMR chemical shift for phenol-urea-formaldehyde prepolymer resin [4,7,8,33-35].

Structure / Group assignment	Chemical shift (ppm)
Unreacted Urea	158-161
Carbonyl C=O	160-163
Cocondensed methylene	48 – 49
Methylene group between phenol	
o – Ph – CH_2 – p - Ph	34.9
p – Ph – CH_2 – p – Ph	39.7 - 40.1
Methylene group between urea	
-NH- CH_2OH	64.8
-N(CH_2-)-CH_2OH	71.4
-N$(CH_2OH)_2$	72.1
Ether group between urea	
-NH-CH_2-O-CH_2-R	67.7
Phenol ring	
Free ortho position	153.1 – 156.2

Free para position	156.2 – 156.8
Ortho and para- substituted position	151.2 – 153.0

M + Na	M + Na	Unit Type

Reactive formaldehyde oligomer	80 - 90

Table 3: Distribution fragment of phenol-urea-formaldehyde (PUF) resin oligomers by MALDI-TOF analysis.

Experimental	Calculated	A	B	
178.29	178	1	1	Ph-CH$_2$-U-CH$_2$
363.51	366	2	2	Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U
		2	2	Ph-CH$_2$-Ph-CH$_2$-U-CH$_2$-U
		2	2	Ph-CH$_2$-U-CH$_2$-U-CH$_2$-Ph
539.36	539	3	3	Ph-CH$_2$-U-CH$_2$- Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U
700.18	701	5	3	Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-U-CH$_2$-U-CH$_2$OH
875.75	879	6	4	Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-U-CH$_2$-U-CH$_2$OH
1037.64	1037	8	4	HO-CH$_2$-U-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-U-CH$_2$-U-CH$_2$OH
1213.36	1215	9	5	Ph-CH$_2$-U-CH$_2$-CH$_2$-U-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-U-CH$_2$-U-CH$_2$OH
1375.03	1373	11	5	HO-CH$_2$-U-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-CH$_2$-U-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-U-CH$_2$-U-CH$_2$-OH
1549.99	1551	12	6	Ph-CH$_2$-U-CH$_2$-CH$_2$-U-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-CH$_2$-U-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-U-CH$_2$-U-CH$_2$-OH
1711.39	1709	14	6	HO-CH$_2$-U-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-CH$_2$-U-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-CH$_2$-U-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-U-CH$_2$-U-CH$_2$-OH
1886.88	1887	15	7	Ph-CH$_2$-U-CH$_2$-CH$_2$-U-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-CH$_2$-U-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-CH$_2$-U-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-Ph-CH$_2$-U-CH$_2$-U-CH$_2$-U-CH$_2$-OH

Note: That Ph = Phenol and U = Urea.