

PROPERTIES OF OIL-PALM-SHELL-BASED PHENOL WOOD ADHESIVES COMPARED WITH PETROLEUM-BASED PHENOL WOOD ADHESIVES

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ABSTRACT

A study was carried out to test the properties of oil-palm-shell-based wood adhesives compared with petroleum-based wood adhesives. Shear strength tests for both dry and wet conditions were done. Besides that, apparent cohesive wood failure tests were also performed to compare the performance of wood bonding between these mentioned adhesives. For the dry test, the bonding performance became better when the formaldehyde to phenol (F/P) ratio increased. For all three different F/P ratios, the petroleum-based adhesives showed the best bonding performance. However, the wood bonding performance of oil-palm-shell-based adhesives was comparable with that of the petroleum-based adhesives. Meanwhile, for the wet test, the bonding performance became better when the F/P ratio increased and the best bonding performance was given by the petroleum-based adhesives with F/P ratios = 1.2 and 1.5. However, it was obvious that the performance of 50% oil-palm-shell-based adhesives was better than that of the petroleum-based adhesives at F/P ratio = 2.0. For apparent cohesive wood failure, the F/P = 2.0 group of samples and the petroleum-based adhesives gave the highest wood failure for all the compositions of adhesives. The commercial potentiality of this research is very high as the oil-palm-shell-based adhesives can replace the petroleum-based adhesives.

Keywords: oil-palm-shell-based adhesives, petroleum-based wood adhesives, shear strength, apparent cohesive wood failure, bonding performance.

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INTRODUCTION

The process of bonding wood materials with glue has been practiced since the early periods of civilization. Early wood adhesives were natural products-based. Animal, casein, soyabean, blood albumin and starch glues were commonly used in quantity in the United States as late as the 1960s. Starches are still used extensively for paper and other industrial applications. Although some natural adhesives, such as casein and modified blood, form a moderately water resistant bond, a truly

waterproof adhesive bond was not available to the wood industry until the advent of various coal tar or petroleum-based synthetic resins in the mid 1930s. The versatile synthetic adhesives, known generically as urea-, melamine-, resorcinol- and phenol-formaldehyde resins, dramatically increased the types and amounts of glued products that could be manufactured. In many respects, today's science of adhesion grew from World War I and II when evaluations were made of the adhesives and gluing processes that were used in constructing wooden aircraft and other war materials.

Phenol formaldehyde (PF) resin has been a commercial synthetic condensate resin since the 1930s. In 1990, its volume as a wood adhesive was second only to that of urea formaldehyde resins worldwide, with about 40% consumed in North

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America. They are the primary binder for exterior applications, such as construction-grade plywood, laminated veneer lumber, oriented strand board and others. PF resins are formulated into two types: one containing molar deficiency of F/P in the presence of acid, or novolac, and the other with molar excess of F/P in the presence of alkaline, or resole. Novolac resin has phenol as the end group and does not have reactive methylol groups unless some hardening or cross-linking agents are added. In other words, these resins are thermoplastic until a cross-linking formaldehyde donor is added, such as hexamethylenetetramine. The novolacs molecular weights range between 200 and 1000. Due to their acidity and initial thermoplastic chemistry, novolac resins have limited applications in wood bonding. One use is for moulded wood-particle products and another is for wafer board face resin. Novolac resins are usually sold in powder form.

The resole resins, both in powder and aqueous forms, have reactive methylol groups that condense into larger molecules when heated without the addition of a hardening cross-linking agent. The heat-cured resole resin is three dimensional, with chemical attachments to wood surfaces that are virtually indestructible. The molecular weights of resole resins may vary from a few hundred to 30 000. In the United States, the resole resins used to bond construction plywood are some of the highest

molecular weight resoles and are water insoluble except in the presence of about 10% to 12% alkalinity on a solid basis. Resole resins, both in powder and aqueous forms, have extensive markets for wood bonding. The typical molar ratio of F/P for plywood resole resin is 1.9 to 2.2:1, the F/P ratio for strand board resole resin is near 2.5:1. For durability in bonding strength, the resole resins are most suitable in the pH range 10 to 11.5. The aqueous forms are shipped with viscosities ranging from 200 to 1200 mPa.s (Pizzi, 1994).

EXPERIMENTAL WORKS

Preparation of Phenolic Resin

Four levels of PF resin replacements with an oil-palm-shell-based phenol were prepared, *i.e.* 25%, 50%, 75% and 100%. It was assumed that the replacement oil-palm-based phenol was as the same as petroleum-based phenol in calculating the mole ratio. The molecular weights of phenol, formaldehyde and sodium hydroxide are 94.11 g mol⁻¹, 30.03 g mol⁻¹ and 40.00 g mol⁻¹ respectively. The petroleum-based PF resin was also prepared. All these PF resins were prepared at three different ratios of F/P = 1.2, 1.5 and 2.0 as shown in *Table 1*.

TABLE 1. VARIABLES IN PHENOL FORMALDEHYDE RESIN FORMULATIONS

Resin sample	Formaldehyde/ phenol ratio	Petroleum-based phenol/ palm-based phenol ratio
PF-01	1.2	100/0
PF-02	1.5	100/0
PF-03	2.0	100/0
PF-04	1.2	75/25
PF-05	1.5	75/25
PF-06	2.0	75/25
PF-07	1.2	50/50
PF-08	1.5	50/50
PF-09	2.0	50/50
PF-10	1.2	25/75
PF-11	1.5	25/75
PF-12	2.0	25/75
PF-13	1.2	0/100
PF-14	1.5	0/100
PF-15	2.0	0/100

Preparation of Test Specimens

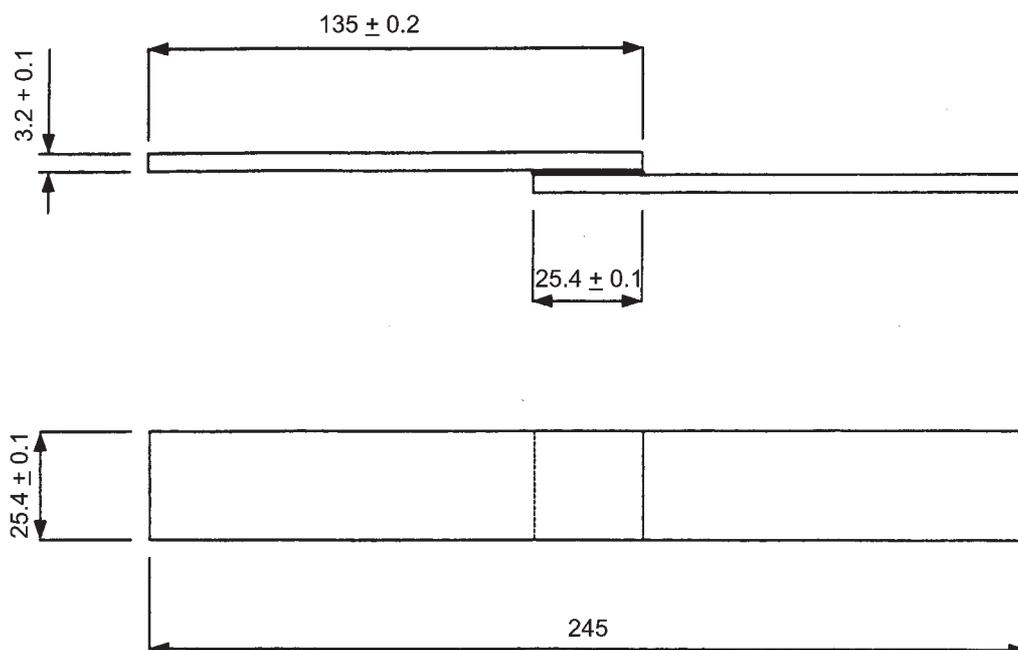
Standard size wood composites used to measure the resin quality were made according to British Standard 1203 (1993c) for phenolic and amino-plastic synthetic resin adhesives for wood. The test specimen was in rectangular form, 135 ± 0.2 mm long in the direction of the face grain and 25.4 ± 0.1 mm wide as shown in Figure 1. It was free of obvious strength-reducing defects. Resin was applied to a 25.4×25.4 mm area at one end of each stick. After an open assembly time of 10 min at ambient conditions, the sticks were lapped over the length of their coated ends. The overlapped sticks were then hot pressed at 200 psi and 160°C for 2.0, 3.5, 5.0 and 7.0 min, using a Carver Laboratory Press, Model C, 12-t capacity, in the polymer laboratory of Universiti Teknologi Malaysia. Four wood composite samples were prepared by the shorter press times and eight composites samples were prepared for the 7.0 min press time. The samples pressed for 7.0 min were separated into two groups, the first group was tested dry and the second was subjected to an accelerated ageing sequence.

quality requirements. For the dry test, after bonding, the test specimens were reconditioned at 51% relative humidity for at least 24 hr prior to mechanical testing. Meanwhile, for the wet test, the test specimens were immersed in boiling water for 4 hr, followed by drying for 20 hr at 60°C and 15 mmHg, and then boiled again for 4 hr (Ono and Sudo, 1989). Finally, the wet test specimens were kept in sealed plastic bags until the mechanical tests.

Bonding Classes

According to British Standard Institution (1993c), there are three classes of bonding quality based upon moisture resistance as follows:

- Class 1: dry conditions. This bonding class is appropriate for normal interior climate.
- Class 2: humid conditions. This bonding class is appropriate for protected external applications, e.g. behind cladding or under roof covering. However, it is capable of resisting weather exposure for short periods,



Note: *All dimensions are in mm.

Figure 1. Example of 2-ply test piece.

Pre-treatment of the Test Specimens

Before the shear strength test, there were two types of pre-treatments, i.e. dry test and wet test, upon the test specimens. These pre-treatments were according to British Standard Institution (1993a) for plywood bonding quality test methods and British Standard Institution (1993b) for plywood bonding

e.g. when exposed during the construction. Besides that, it is also suitable for interior situations where the service moisture condition is raised above the Class 1 level.

- Class 3: exterior conditions. This bonding class is designed for exposure to weather over sustained periods. Thus, the Class 3 level of

bonding performance is better than the previous classes.

As described before, the wet test pre-treatment can fulfil the Class 3 bonding quality if they reach certain requirements. For all three bonding classes, each glue-line should satisfy two criteria, *i.e.* the mean shear strength and the mean apparent cohesive wood failure as combined in Table 2. The relationship between the mean percentage of apparent cohesive wood failure and the mean shear strength given in Table 2 is illustrated in Figure 2.

Method for Determination of Failing Force and Shear Strength

Owing to the non-axial transmission of applied force through the prescribed test pieces and the consequent tendency for the test pieces to bend during pulling, the strength developed on the test joints is influenced by the extent of the bending. Testing machines vary widely in this respect. In order to obtain comparable test results, it is necessary to specify the rate of straining or the rate of increase of force and the type of jaw assembly to be used.

TABLE 2. REQUIREMENTS FOR WOOD BONDING QUALITY

Mean shear strength, f_v (N mm ⁻²)	Mean apparent cohesive wood failure, w (%)
$0.2 \leq f_v \leq 0.4$	≥ 80
$0.4 \leq f_v \leq 0.6$	≥ 60
$0.6 \leq f_v \leq 1.0$	≥ 40
$1.0 \leq f_v$	No requirement

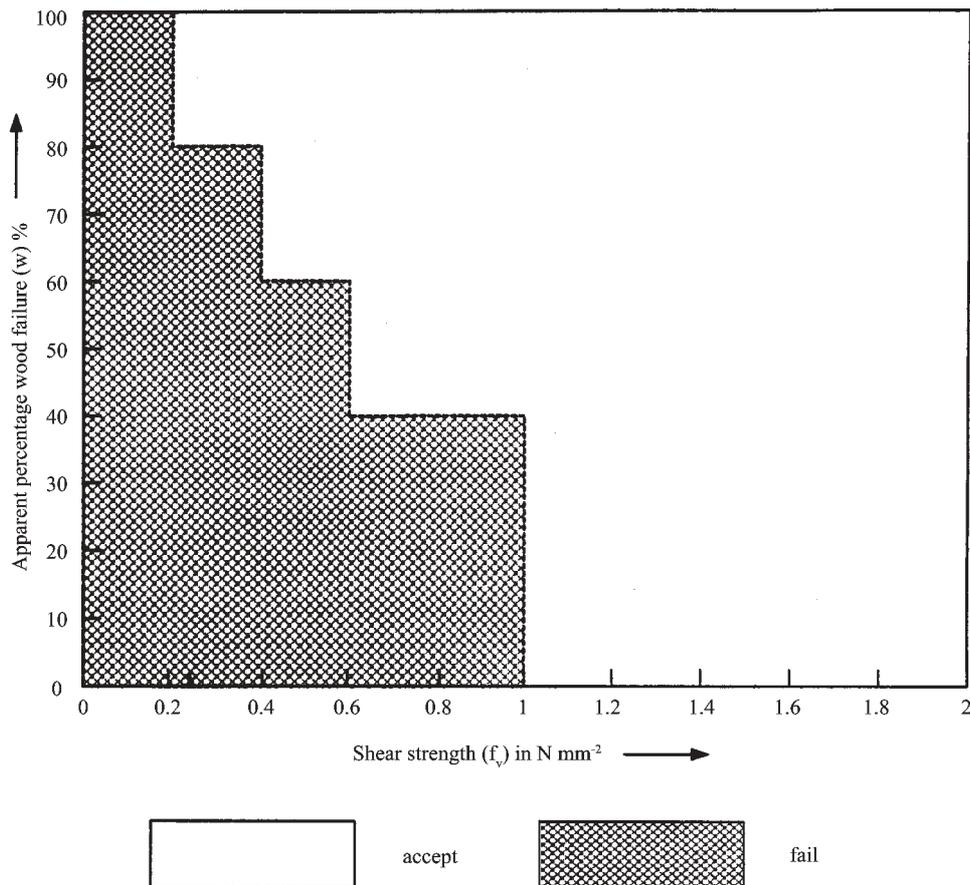


Figure 2. Relationship between the mean percentage of apparent cohesive wood failure and the mean shear strength.

For the rate of application of force with the test piece in position and under applied force, there are two different methods as described (British Standard Institution, 1979; Malaysian Standard Institution, 1984; Malaysian Standard Institution, 1991):

- in the testing machines provided with a means of controlling the rate of increase in force, the rate of increase in force was between 1.3 kN min^{-1} and 2.7 kN min^{-1} ; and
- in the testing machines where control is of the rate of separation of the straining head, this rate of separation was between 6 mm min^{-1} and 12 mm min^{-1} .

Meanwhile, for the type of jaw assembly, the jaws gripped the test piece with a wedge action. Each pair of jaws was attached by loose fitting pin joints which, in turn, were fitted by ball-and-socket joints to the straining heads. In a mounted horizontal machine, the dead weight of the jaw assembly was carried by freely moving cross-members. This did not affect the freedom of the jaws. Alternatively, one of the pairs of jaws was suspended from a ball-and-socket joint allowing sufficient sideway movement of the jaw to permit its self-alignment of this jaw whilst the test pieces were being pulled.

Before operating, the machine was adjusted to operate at not exceeding 5.5 kN. The test piece was inserted so that the length between the wedge grips was within the range 45 mm to 55 mm. In this research, the shear strength was measured with a high performance Instron testing machine, model 5567, in the polymer laboratory of Universiti Teknologi Malaysia. The alignment and jaw setting had to be adjusted before the specimen was inserted. The specimen had to be inserted squarely in relation to the direction of pull, and care had to be taken not to knock or displace the jaws during the specimen insertion in such a way that excessive stress or stress in the wrong plane was put on the specimen. If one set of jaws was fixed and the other floating, the specimen should be inserted in the floating jaw first. The distance between the wedge grips of the test piece was 46 mm, with the specimen mounted centrally. After that, the force was applied by the rate of separation of the straining head of 9 mm min^{-1} until the test piece was broken. The maximum load in Newtons for breaking the test piece was recorded and printed. The shear strength f_v for each test piece in N mm^{-2} was calculated from the following formula (Timings, 1998):

$$f_v = \frac{F}{l \times w} \quad (5-1)$$

where F is the failing force of the test piece, in Newtons;

l is the length of the shear area, in mm; and
 w is the width of the shear area, in mm.

After this, each specimen was examined when its surface was dry to determine the percentage wood fibre on the failed surface. The failure should normally have occurred in the wood that was within the shear test area. When the failure occurred outside the test area, or if by cross-grain breaking 50% or more of the surface of a face veneer, the result was rejected and the test repeated. If the number of test pieces rejected exceeded 20%, it was necessary to resample. If the resampling was also rejected on this basis, then the batch was rejected. The test pieces were allowed to dry before determination of the apparent cohesive wood failure.

Method for Determination of Apparent Cohesive Wood Failure

The apparent cohesive wood failure was visually estimated based on ASTM D 5266, the American Society for Testing and Materials (1999) standard procedure for estimating the percentage of wood failure in adhesive bonded joints. Wood failure is defined as the rupturing of wood fibre in strength tests on bonded specimens, usually expressed as the percentage of the total area involved which shows such failure. Wood failure is one of the principal means for determining the quality of an adhesively bonded wood joint. When evaluated after water soaking and drying, or boiling and drying, the percentage of wood failure is an important criterion for qualifying adhesives for use in plywood and glued laminated structural timber for exterior use, and for daily quality control of the processes for manufacturing plywood and glued, laminated timbers.

Various light sources have been found useful in estimating wood failure. In determining the standard specifications, the source must be chosen by the user of this practice as listed:

- dual-element fluorescent desk lamp equipped with one 15 Watt daylight and one 15 Watt cool white tube;
- circular fluorescent desk lamp with 5X viewing magnifier in the centre of the lamp; and
- diffuse natural light from a window facing away from the sun.

Besides the light sources, a ruler with 2.54 mm or 0.1 inch divisions is recommended as an aid for estimating the area of torn wood fibre. A transparent template of the size of the specimen bonded area and scribed with various shapes and areas with known percentages of the total area, is also useful for subdividing the area. Another important apparatus is a low power magnifying glass of 3 to 5X, with a field of view able to encompass most of the failed surface, which may be use for inspecting areas where shallow wood failure is suspected.

If the specimens were tested in wet condition, the failed surfaces were dried in an air-circulating oven at 71°C, or under equivalent conditions, before estimating the percentage of wood failure. The working procedure was as follows:

- the experiment was conducted in a location where direct outside light did not fall on the specimen;
- diffused natural light from a window facing away from the sun was chosen and used consistently;
- the specimens were half opened, as you would open a book;
- plywood specimens were held with their long dimension perpendicular to the line between the light source and the eye;
- the tilt of the specimen was varied as shown in the side view in *Figure 3*, so that the area of wood and adhesive failure can be distinguished. Care had to be taken in order not to create shadows, especially in the case of deep wood failure;
- the wood failure was shallow when there was little colour contrast between the wood and the adhesive. Special measures may be required. Magnification, rotation of the specimen, and variation of the incident angle

- of the light on the surface were often necessary to distinguish shallow wood failure from adhesive failure, especially when the adhesive was light coloured or transparent;
- if the specimen was rotated to detect shallow wood failure, the specimen was always repositioned in the standard position when making the estimate of wood failure;
- if there were scattered areas of shallow wood failure, the loose fibre was blown or brushed from the surface. Wood failure was counted on areas with wood cells that actually adhere to the adhesive;
- the total percentage of wood failure was estimated using a ruler or scribed transparent template;
- the surface was divided into quadrants for estimating the areas of various forms of failure. Wood failure was estimated on both halves of the specimen, but the wood failure from matching areas more than once was not counted. Alternatively, the wood failure percentage on both halves of the specimen was read and divided by the sum of 2; and
- total wood fibre failure of each specimen was estimated with a maximum of 100% of the total bonded test area.

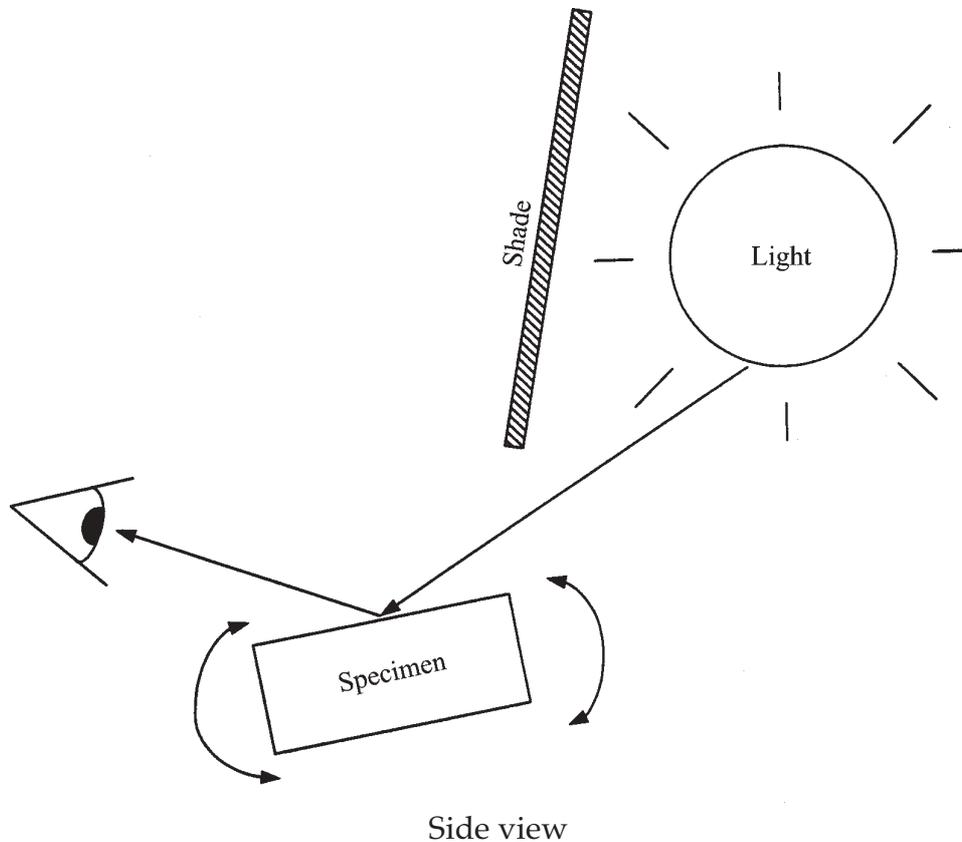


Figure 3. Positioning of test pest specimen in relation to the light source and eye.

RESULTS AND DISCUSSION

Shear Strength

Shear strength of phenolic resin for formaldehyde to phenol (F/P)=1.2 by dry test. The shear strengths of phenolic resin for F/P ratio = 1.2 for different pressing times are shown in Figure 4. The 0% represents petroleum-based phenolic resin and 100% represents 100% oil-palm-shell-based phenolic resin. Meanwhile 25% represents 25% replacement of petroleum-based phenol with oil-palm-shell-based phenol, and so on. The performance of the petroleum-based phenolic resin was better than the oil-palm-shell-based phenolic resin. From Figure 4, it can be concluded that all the adhesive performances were acceptable except for the specimen with 0% at 2 min pressing time as its $f_v < 1.0 \text{ N mm}^{-2}$ as described in Figure 2.

Shear strength of phenolic resin for formaldehyde to phenol (F/P)=1.5 by dry test. The shear strengths

of phenolic resin for F/P ratio = 1.5 for different pressing times are shown in the Figure 5. The performance of the petroleum-based phenolic resin was better than that of the oil-palm-shell-based phenolic resin. From Figure 5, it can be concluded that all the adhesive performances were acceptable except for the specimen with 50% at 2 min pressing time as its $f_v < 1.0 \text{ N mm}^{-2}$.

Shear strength of phenolic resin for formaldehyde to phenol (F/P)=2.0. The shear strengths of phenolic resin for F/P ratio = 2.0 for different pressing times are shown in Figure 6. The performance of the petroleum-based phenolic resin was better than that of the oil-palm-shell-based phenolic resin. From Figure 6, it can be concluded that all the adhesive performances were acceptable except for the specimens of 50% and 100% at 2 min pressing time as their $f_v < 1.0 \text{ N mm}^{-2}$.

Shear strength of different phenolic resin by wet test. The shear strengths of different phenolic resins by

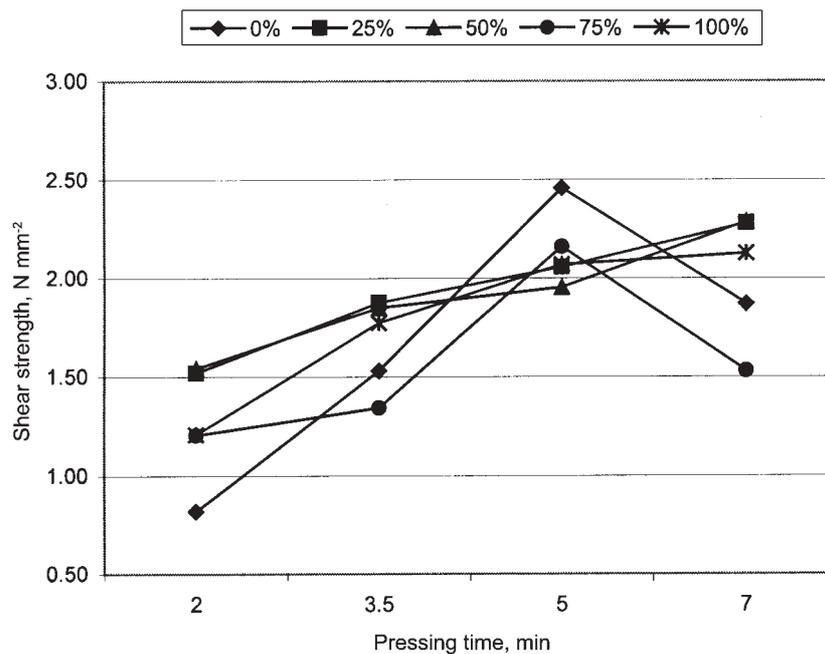


Figure 4. Shear strength of different phenolic resins for formaldehyde to phenol (F/P)=1.2.

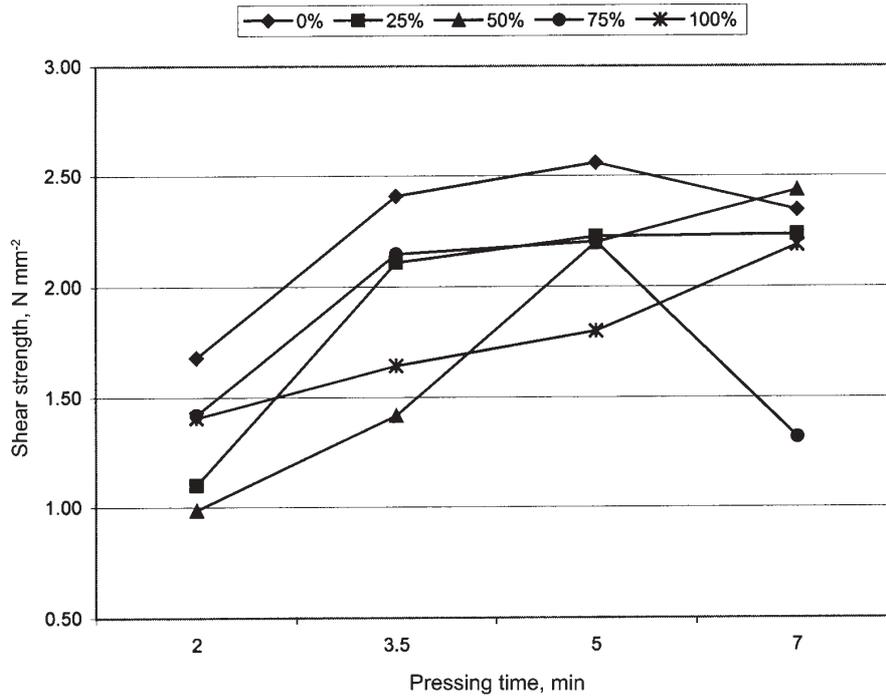


Figure 5. Shear strength of different phenolic resins for formaldehyde to phenol (F/P)= 1.5.

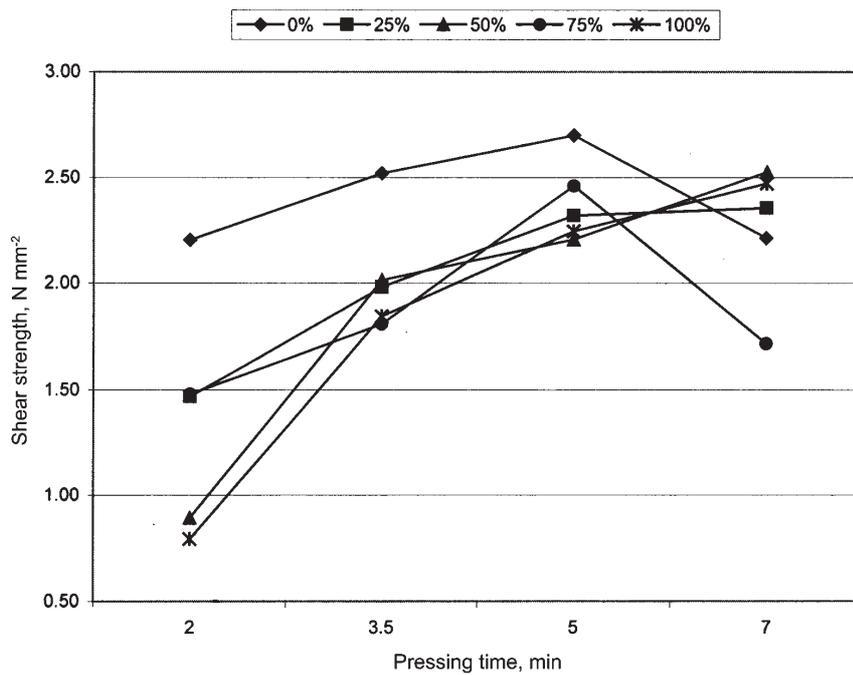


Figure 6. Shear strength of different phenolic resins for formaldehyde to phenol (F/P)= 2.0.

the wet test are shown in the Figure 7. For the wet test, the results showed that the shear strengths increased with the F/P ratio. The maximum shear strengths were laid on the specimen of 50% at F/P = 2.0. It can be concluded that all of the adhesive performances were acceptable as their $f_v > 1.0 \text{ N mm}^{-2}$.

Maximum shear strength of phenolic resin for dry test and wet test. For the dry test, the maximum

shear strengths of the phenolic resins are shown in Figure 8. From Figure 8, the bonding performance became better when the F/P ratio was increased. Besides that, the best bonding performance was given by the petroleum-based phenolic resin for all three different F/P ratios. However, it was obvious that the performance of oil-palm-shell-based phenolic resin was comparable or even as good as that of the petroleum-based phenolic resin. The

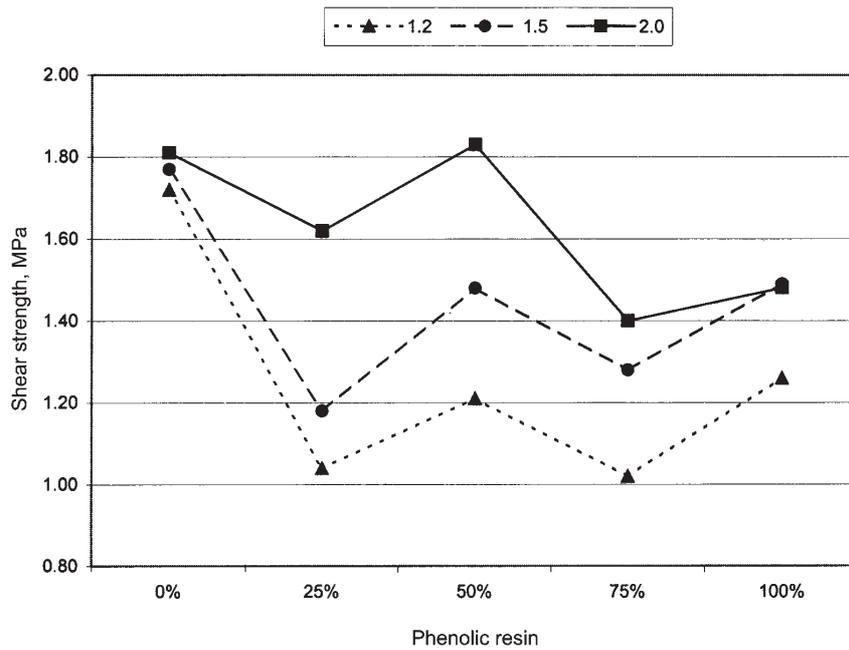


Figure 7. Shear strengths of different phenolic resins by the wet test.

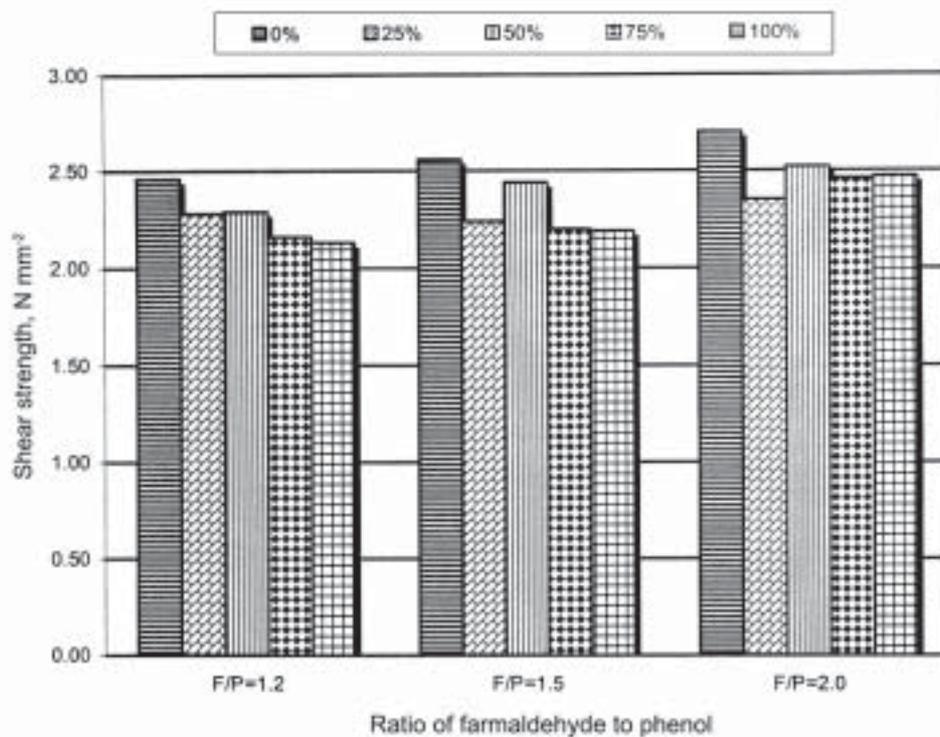


Figure 8. Shear strengths for five different percentage phenolic resins (dry test).

average difference in bonding performance percentage between the oil-palm-shell-based with the petroleum-based phenolic resin was not so high, i.e. 10%, 11%, and 9% for F/P = 1.2, 1.5 and 2.0, respectively.

Meanwhile, for the wet test, the shear strengths of the phenolic resins are shown in Figure 9. From

Figure 9, the bonding performance became better when the F/P ratio was increased. The best bonding performance was given by the 50% oil-palm-shell-based phenolic resin at F/P ratio = 2.0. It was also significant to note that all of the oil-palm-shell-based adhesives shear strengths were more than 1.0 N mm⁻², the border line for acceptance of bonding performance.

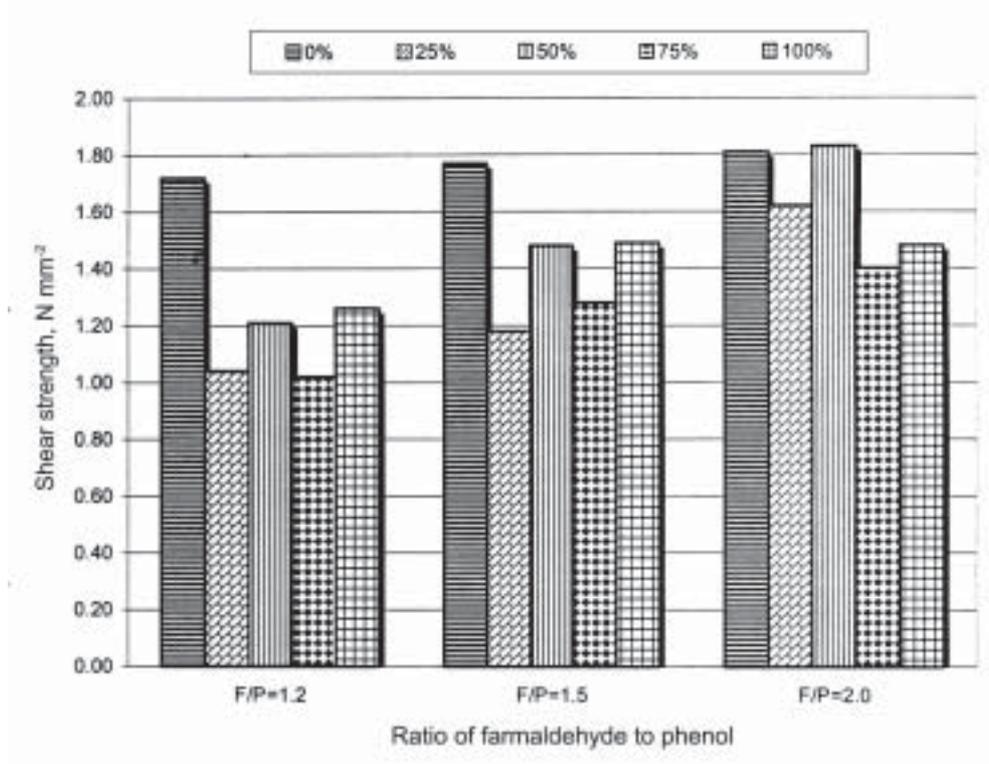


Figure 9. Shear strengths for five different percentage phenolic resins (wet test).

Wood Failures of Phenolic Resin for Dry Test and Wet Test

Figure 10 shows the results of apparent cohesive wood failure of the phenolic resin samples that had maximum shear strengths. From Figure 10, the F/P = 2.0 group of samples gave the highest wood failure

for all compositions of phenolic resin. Among these samples, the petroleum-based phenolic resin showed the highest wood failure. These results matched those from the shear strength tests. Therefore, it can be concluded that higher bonding performance gave higher wood failure percentage.

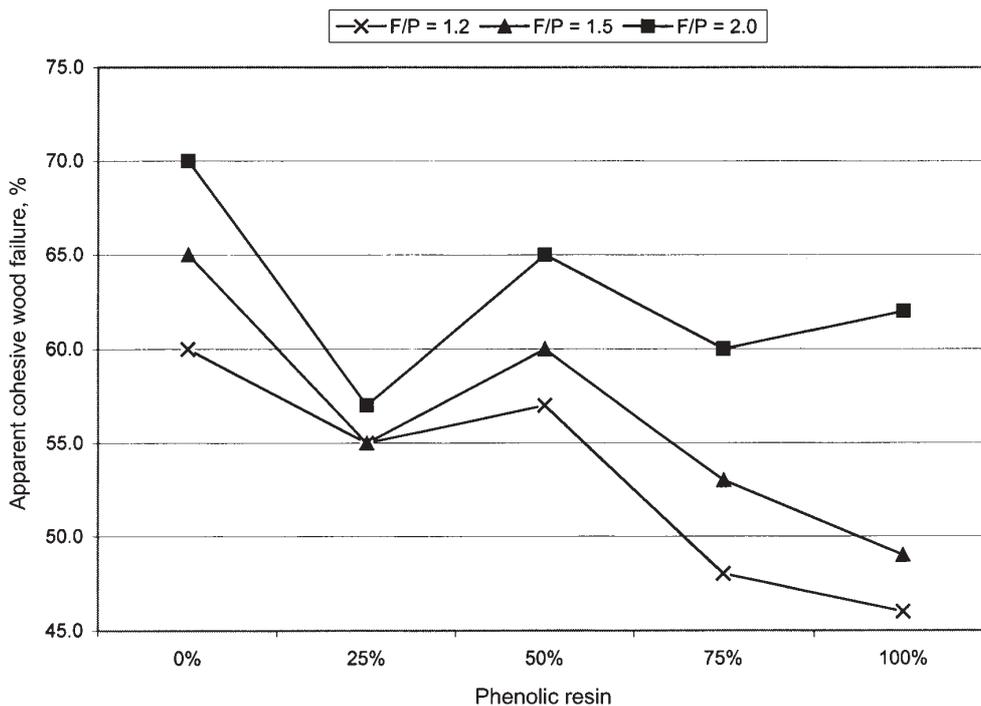


Figure 10. Apparent cohesive wood failure for the dry test.

At the same time, the results of apparent cohesive wood failure of the wet test are showed in *Figure 11*. From *Figure 11*, it shows that the F/P = 2.0 group of samples gave the highest wood failure for all compositions of phenolic resin. Though the petroleum-based phenolic resin showed quite high wood failure, the 50% samples at F/P = 1.5 and 2.0 were higher than them. It showed that the oil-palm-shell-based phenolic resins were as good or even better than the petroleum-based phenolic resin in the wet test.

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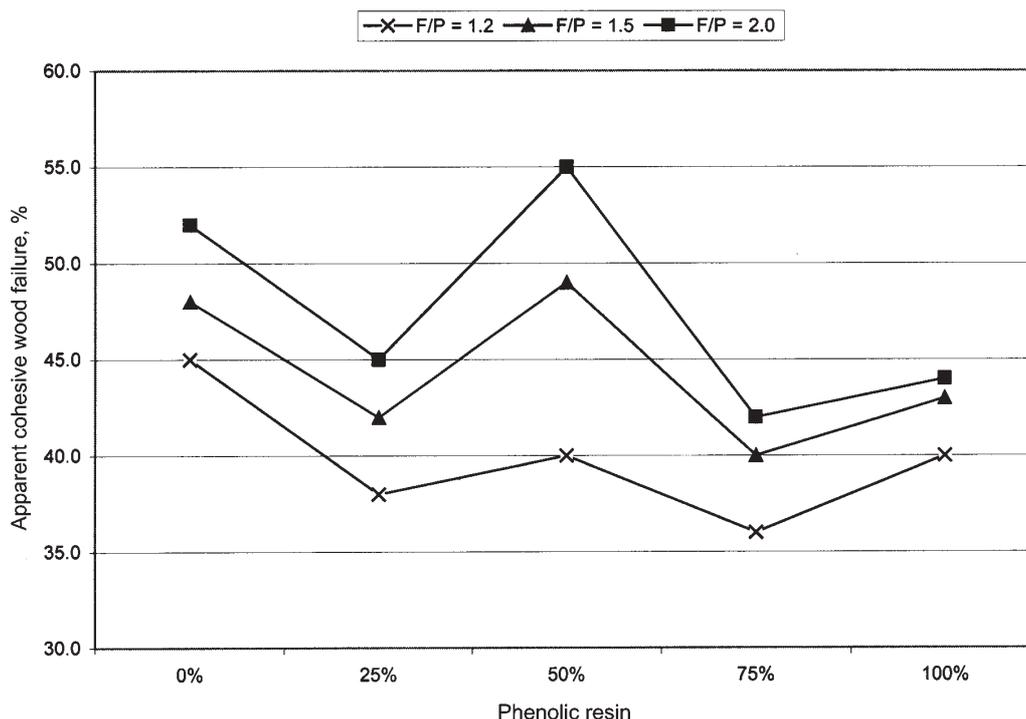


Figure 11. Apparent cohesive wood failure for the wet test.

CONCLUSION

To compare the wood bonding performance between petroleum-based adhesives with oil-palm-shell-based adhesives, it was found that their performances were comparable and acceptable. For the dry test, the average difference percentage in bonding performance between the oil-palm-shell-based with the petroleum-based phenolic resin was not so high, *i.e.* 10%, 11%, and 9% for F/P = 1.2, 1.5 and 2.0, respectively. As for the wet test, the oil-palm-shell-based adhesives showed even better results than the petroleum-based adhesives in certain situations. From the apparent cohesive wood failure, the higher bonding performance gave higher percentage wood failure. Thus, it can be concluded that the oil-palm-shell-based phenol can replace partly or totally the petroleum-based phenol in wood bonding adhesives.

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