

SURFACE ACTIVATION WITH LITHIUM AND SODIUM HYDROXIDES ON REGROWTH KARRI AND JARRAH

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JAMAL BALFAS. 1994. Surface activation with lithium and sodium hydroxides on regrowth karri and jarrah. Surface activation using lithium and sodium hydroxides was examined to determine its effect on wettability and gluebond strength of regrowth karri (*Eucalyptus diversicolor*) and jarrah (*E. marginata*). Wood blocks were treated with three different concentrations of each hydroxide prior to gluing with resorcinol formaldehyde resin. Glued blocks were pressed at 1500 kPa and 20°C for 7 h. Contact angle and shear strength were measured to assess the effectiveness of the treatment. Both lithium and sodium hydroxides significantly increased wettability and dry shear strength of the two regrowth eucalypts. These effects varied according to wood type, solution concentration and type of hydroxide. Bond strengths of treated specimens increased to a greater degree in jarrah than in karri. Increases in solution concentration significantly increased dry bond strength, but in most cases also increased the strength loss during wetting. Lithium hydroxide gave higher improvement in both dry and wet bond strengths than sodium hydroxide. Treatment using 0.5 M lithium hydroxide was the most effective method to protect strength loss on wetting.

Keywords: Jarrah - karri - resorcinol formaldehyde - lithium hydroxide - regrowth - shear strength - sodium hydroxide - surface activation - wettability

JAMAL BALFAS. 1994. Pengaktifan permukaan dengan lithium dan sodium hidroksida ke atas pertumbuhan balik karri dan jarrah. Pengaktifan permukaan dengan penggunaan lithium dan sodium hidroksida telah di kaji untuk menentukan kesannya ke atas pembasahan dan kekuatan perekat pada pertumbuhan balik karri (*Eucalyptus diversicolor*) dan jarrah (*E. marginata*). Blok kayu telah di rawat dengan kedua-dua hidroksida ini pada tiga kepekatan yang berbeda sebelum direkat dengan resorcinol formaldehyde. Blok yang telah di rekat di tekan pada 1500 kPa dengan suhu 20°C untuk 7 jam. Sudut sentuhan dan kekuatan ricih di ukur untuk menentukan keberkesanan rawatan. Lithium dan sodium hidroksida meningkatkan darjah pembasahan dan kekuatan ricih kering bagi kedua eucalypt. Nilai keberkesanan ini berubah mengikut jenis kayu, kepekatan larutan dan jenis hidroksida. Kekuatan rekatan specimen yang dirawat meningkat dengan libih tinggi padajarah berbanding dengan karri. Peningkatan kepekatan larutan meningkatkan kekuatan rekatankeringdengan ketara, tetapi dalam kebanyakan kes ia juga meningkatkan kekuatan yang hilang semasa pembasahan. Lithium hidroksida memberikan kekuatan rekatan kering dan basah yang lebih baik dari sodium hidroksida. Rawatan 0.5 M lithium hidroksida merupakan kaedah yang paling berkesan untuk melindungi kekuatan yang hilang semasa pembasahan.

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Introduction

Surface treatment using sodium hydroxide (NaOH) to improve adhesion was first described by Truax in 1929. He found that certain species of timber treated with a 10% solution of caustic soda and glued with casein glue resulted in improved joint strength. Chen (1970) varied this method using a wide variety of tropical species bonded with urea formaldehyde and resorcinol formaldehyde. He also found that chemical treatment significantly improved wettability and adhesion strength in tested species. Recent studies using both hardwoods and softwoods have all confirmed the beneficial effect of sodium hydroxide in wood bonding (e.g. Wellons 1980, Young *et al.* 1985, Gardner & Elde 1988).

Surface activation with sodium hydroxide modifies the wood surface by reducing surface tension, removing extractives and increasing the ability of the adhesive to dissolve extractive materials on the surface (Wellons 1980). However, this activation may swell the wood surface extensively, or even disintegrate it to some extent and cleave some of the hydrogen bonds of cellulose, which results in a high dry shear strength with no water resistance (Young *et al.* 1985). This indicates the beneficial effect of NaOH treatment to improve the performance of glued timber joint in interior uses, but not for outdoor uses.

Lithium hydroxide (LiOH) differs from sodium hydroxide in its reaction towards weak acids, and its salts are more stable and less soluble in water than sodium salts (Cotton & Wilkinson 1980). Since wood extractives as an important surface inactivating agent contain a large amount of weak acids, it is possible that surface activation using lithium hydroxide could produce a different modification at wood surface compared to sodium hydroxide. In theory, lithium hydroxide has a greater ability to accelerate the curing of phenolic resins than sodium hydroxide (Subramanian 1984). However, a preliminary observation using scanning electron microscopy on wood laminates treated with lithium and sodium hydroxides suggested that the two chemicals had similar swelling effect at wood surface (Balfas & Heady, unpublished data). The aim of this study was to determine whether surface activation using lithium hydroxide can give a comparable bonding improvement to that achieved with sodium hydroxide.

Materials and methods

Sample preparation

Samples used in this study consisted of defect-free, flatsawn heartwood of regrowth karri (*Eucalyptus diversicolor*) and jarrah (*E. marginata*), the two principal commercial species of Western Australia. Fifty sample boards each of karri and jarrah measuring 10 × 100 × 600 mm were provided by the Department of Conservation and Land Management (CALM), Western Australia. The karri boards were relatively uniform in colour but there were distinct colour differences between the jarrah boards. Since colour differences in wood may indicate differences in extractive content (Haygreen & Bowyer 1985) which may in turn

influence glue bonding (Chugg 1964), it was decided to subdivide the jarrah boards into three groups of light, medium, and dark colour respectively. All boards were replaned on both sides to 8 mm thickness to give a fresh surface, then cut into small blocks measuring 8 mm radial \times 25 mm longitudinal \times 100 mm tangential (Figure 1). After cutting, wood blocks were conditioned to 10 - 11% moisture content in a conditioning room at $20 \pm 1^\circ\text{C}$ and $65 \pm 5\%$ relative humidity for three weeks. Seventy wood blocks of each sample type were selected randomly and divided into seven groups, *i.e.*, 10 blocks per group, one group as control, the others treated separately with three different concentrations, *i.e.*, 0.5, 1.0 and 2.0 M solutions respectively of lithium hydroxide and sodium hydroxide. Both sides of each treated block were smeared with the corresponding solution at the rate of $120 \mu\text{l}$ per 2500 mm^2 (48 ml m^2), one face prepared for wettability determination and the other for bonding experiment. The required amount of chemical solution was accurately placed on the wood surface by means of a syringe and the solution spread evenly with a fine glass rod. After treatment the wood blocks were conditioned as above for 24 h prior to wettability measurements.

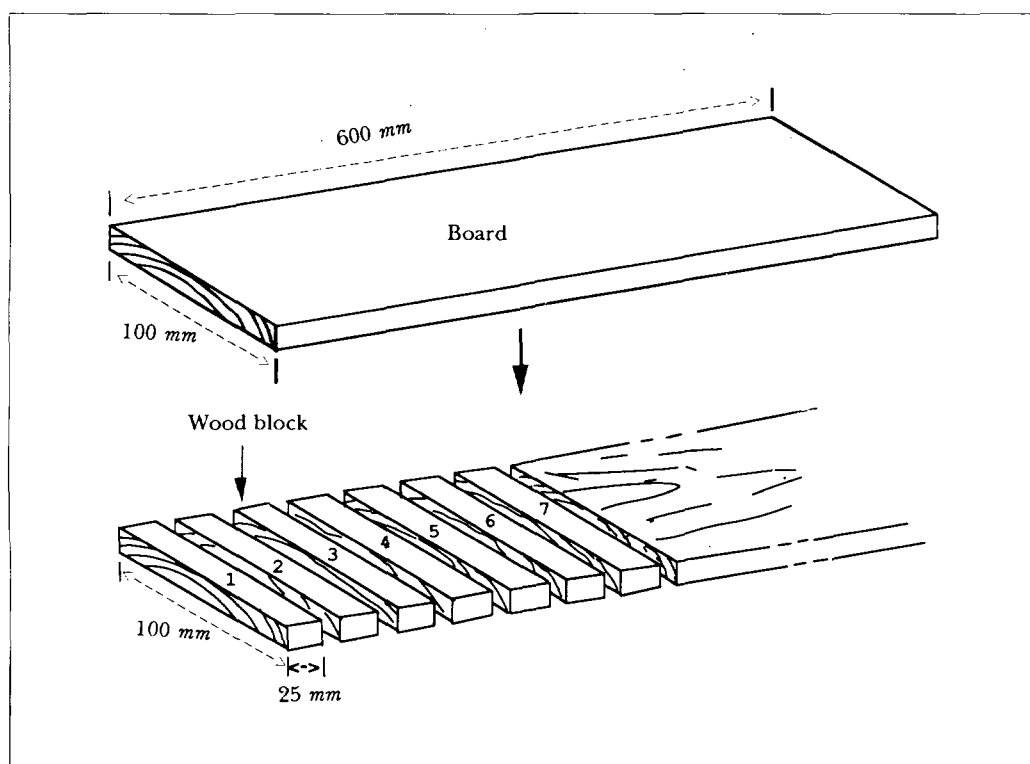


Figure 1. Cutting arrangement from board into small blocks

Extractives and specific gravity determination

Five new blocks from each sample type were selected at random and ground into 60 - mesh wood flour. Solubility in 0.5 % solution of sodium hydroxide was

determined using the method of Cohen and Dadswell (1931). The specific gravity of the wood for each sample type was determined using the method described by Haygreen and Bowyer (1985). For this determination ten smaller blocks measuring $8 \times 25 \times 25$ mm were used.

Swelling measurement

Five wood blocks from each type of sample were cut into ten wood sticks measuring 6 mm (longitudinal), 10 mm (radial) and 100 mm (tangential). The sticks were then placed in the conditioning room for one week before testing. Tangential swelling tests of the specimens in water were undertaken according to ASTM Standard D4446 - 84, with some modifications to the swellometer apparatus. The tangential side of each test specimen was inserted between the guides of the swellometer so that one end was firmly in contact with the adjustable base of the swellometer and the other end was in contact with the plunger of the dial gauge. A dial reading (R1) was recorded before immersing the sample in distilled water, and again after 24 h immersion (R2). Swelling rate was calculated by dividing the reading difference (R2- R1) to the tangential dimension and multiplied by 100.

Wettability measurement

With some modifications the method described by Gray (1961) was used in this study to determine the wettability of the control (untreated) and treated surfaces. The modifications used were as follows: instead of a horizontal microscope, a vertical microscope with a goniometer eyepiece was used for measuring the advancing contact angle of a distilled water drop placed on the wood surface; in place of a rotating stage, a horizontal jig was used to place and move the specimen; a 10 μ l drop of distilled water was placed on the wood surface using a syringe; the wetting angle was measured within 10 sec using the goniometer eyepiece. Five drops were placed on each wood block, hence fifty measurements were recorded for each treatment. Wettability was expressed as the cosine of the advancing contact angle.

Gluing procedures

After calculating the average wettability of each wood block, samples were arranged into five pairs on the basis of the similarity of their wettability measurements. Five small panels were made for each sample type and treatment group by bonding a pair of wood blocks parallel to the grain. Resorcinol formaldehyde resin (winter grade Bontite - 145 plus hardener) was used as the adhesive. The resin and hardener were accurately mixed by weight in the ratio of five parts resin to one part hardener. A fresh mixture of adhesive was applied to each surface by means of a small plastic roller at a spread rate of 1.2 mgmm^{-2} . The amount of adhesive was determined by weighing the wood block before and after gluing with a digital electronic balance (Ainsworth AL-300). The total (open and closed) assembly time was less than 8 min. The bonded area of each surface was 2000

mm^2 , i.e., 100 mm (tangential) by 20 mm (longitudinal). The five small panels were clamped in five different presses located in the conditioning room (Figure 2). Presses were calibrated to give a pressure of 1500 kPa. Clamping was effected by pressing the rocker head of the press down with a calibrated torque wrench; a pressure of 1500 kPa being maintained for 7 h as recommended by the adhesive manufacturer. After this period, the panels were removed from the presses, but they remained in the conditioning room (as above) to cure for a further seven days prior to testing.

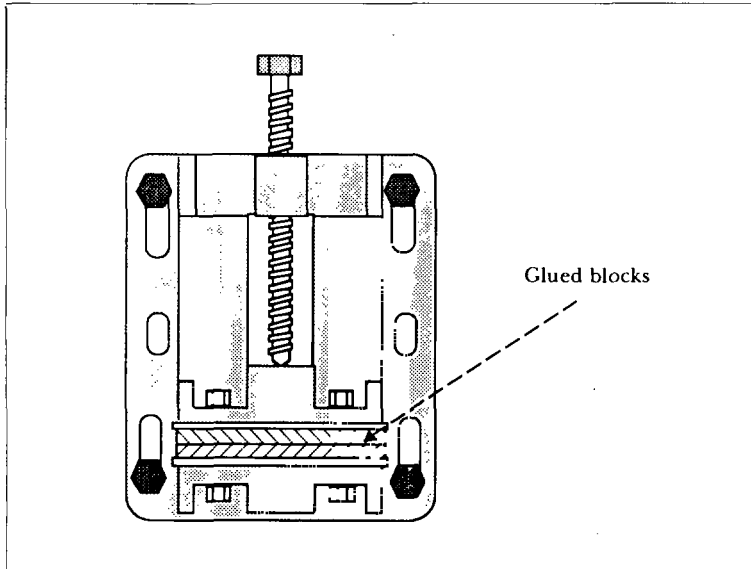


Figure 2. Small press used for clamping the glued blocks

Shear strength determination

Each glued block was cut with a small bandsaw (1 mm kerf) into four shear test specimens (Figure 3), and dressed to a final 23 mm width with a disc sander. Consequently, 20 shear blocks were made for each treatment and wood type, and then divided into two sub-groups, one sub-group was tested in dry condition and the other after 24 h immersion in water at room temperature. Shear strength was determined according to the modified ASTM D905 as described by Strickler (1968). The shear area of each specimen was 460 mm^2 . The specimen was held on a Shimadzu Universal Testing Machine by means of a shear test jig. Load was applied at a constant strain rate of 0.4 $mm\ min^{-1}$. The force at failure was recorded and shear strength was calculated as follows:

$$S = F/A,$$

where: S = Shear strength (MPa)

F = Force at failure (N)

A = Shear area (460 mm^2)

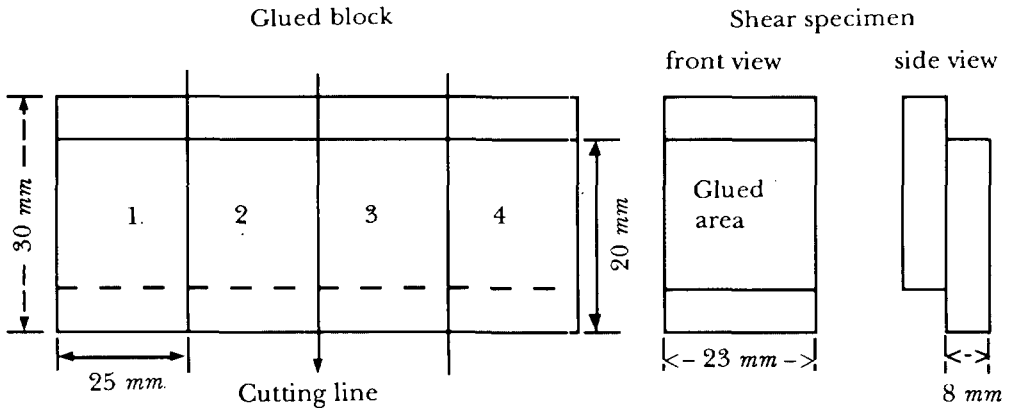


Figure 3. Shear test specimen arrangement

Results and discussion

The average extractives content, specific gravity and tangential swelling of wood samples are shown in Table 1. Karri had significantly ($p < 0.05$) lower extractives content but higher specific gravity and tangential swelling than jarrah. Since there were no significant differences in such basic properties between medium and dark jarrah at 5% probability level, the two types of sample were then combined and designated as dark jarrah.

Table 1. Extractives content, specific gravity and tangential swelling of wood samples

Wood type	Extractives content (%)	Specific gravity	Tangential swelling (%)
Karri	17.89 (0.38)*	0.669 (0.034)*	8.12 (1.10)*
Light jarrah	21.30 (0.42)	0.584 (0.017)	6.23 (1.14)
Medium jarrah	23.22 (0.63)	0.637 (0.023)	5.48 (0.41)
Dark jarrah	22.63 (0.20)	0.641 (0.015)	5.34 (0.66)

* Standard deviation in parentheses.

The untreated specimens of karri had wettability value of 0.175 which is higher than 0.029 - 0.055 for jarrah (Table 2). In fact, some specimens of light and dark jarrah had contact angles greater than 90° or had negative wettability values. Previous studies have shown that wood extractives greatly influence wettability of wood surfaces (e.g., Gray 1961, Chen 1970, Jordan & Wellons 1977). Thus the lower wettability of jarrah may be related to its higher extractives content.

Both lithium and sodium hydroxides had significant ($p < 0.01$) effect on the wettability of karri and jarrah (Table 2). For sodium hydroxide treatment, the wettability of wood surfaces increased with increasing NaOH concentration. Conversely, wettability improvement on wood surface treated with lithium hydroxide decreased with its increasing concentration. The precise reasons for this disparity are not known. Distilled water used for wettability measurements may react differently with the lithium and sodium salts. Cotton and Wilkinson (1980) state that lithium salts of weak acids are less reactive to water than sodium salts. Thus lithium salts formed by weak acids of wood extractives might be responsible for the decreased wettability with increasing lithium hydroxide concentration.

Table 2. Wettability of the untreated and treated karri and jarrah

Treatment	Wettability (Cos θ)		
	Karri	Light jarrah	Dark jarrah
Untreated	0.175 (0.014)*	0.029 (0.068)*	0.055 (0.030)*
0.5 M LiOH	0.701 (0.062)	0.643 (0.022)	0.637 (0.094)
1.0 M LiOH	0.624 (0.139)	0.388 (0.119)	0.412 (0.103)
2.0 M LiOH	0.606 (0.080)	0.120 (0.020)	0.296 (0.047)
0.5 M NaOH	0.706 (0.021)	0.580 (0.034)	0.514 (0.023)
1.0 M NaOH	0.788 (0.009)	0.700 (0.020)	0.699 (0.037)
2.0 M NaOH	0.796 (0.007)	0.737 (0.038)	0.732 (0.030)

*Standard deviation in parentheses.

Dry shear strength of the untreated karri (10.16 MPa) was significantly ($p < 0.01$) higher than those of the untreated light jarrah (6.95 MPa) and dark jarrah (6.67 MPa) (Table 3). The higher bond strength of karri might be related to its lower extractives content than that of jarrah (Table 1). A number of authors (e.g., Chen 1970, Plomley *et al.* 1976, Young *et al.* 1985, Hillis 1986) have suggested that extractives could interfere with the process of adhesive bond formation by forming a barrier at the glue-wood interface that prevents adequate wetting, or causes mechanical weakness. These effects could alter the normal flow and spread of the adhesive on wood surface which in turn prevents the cure of the adhesive. In contrast, the glued untreated karri laminates had wet shear strength of 2.50 MPa which was markedly lower than that for jarrah (5.44-5.95 MPa). This indicates a greater strength loss in karri laminates during 24 h immersion than in jarrah laminates. Bond strength losses during wetting are particularly caused by weakening of the glue bond due to stresses developed as a result of dimensional changes in the wood laminates. Since the glueline restrains the free dimensional changes, shear stresses may develop between laminae which can produce sufficient force to separate a weaker glueline (Bodig 1982). The higher strength loss in karri specimens may be due to its lower dimensional stability than in jarrah, as indicated by its greater tangential swelling (Table 1).

Table 3. Dry and wet shear strengths of the untreated and treated karri and jarrah

Wood type	Concentration (M)	LiOH treated			NaOH treated		
		Shear strength (MPa)		Strength loss (%)	Shear strength (MPa)		Strength loss (%)
		Dry	Wet		Dry	Wet	
Karri	0 (Control)	10.16 (1.69)	2.50 (2.36)	75.39	10.16 (1.69)	2.50 (2.36)	75.39
	0.5 M	12.09 (2.14)	10.94 (1.37)	9.52	11.88 (2.29)	6.11 (1.85)	48.55
	1.0 M	12.74 (2.00)	11.14 (0.21)	12.59	12.09 (2.30)	5.70 (4.98)	52.88
	2.0 M	15.46 (3.14)	8.71 (1.35)	43.67	14.34 (1.25)	4.29 (3.69)	70.12
Light jarrah	0 (Control)	6.95 (1.36)	5.44 (4.65)	21.63	6.95 (1.36)	5.44 (4.65)	21.63
	0.5 M	14.73 (3.93)	12.86 (0.93)	12.72	13.67 (4.22)	10.58 (2.07)	22.58
	1.0 M	15.91 (4.12)	11.19 (2.49)	29.67	14.18 (2.06)	10.61 (2.26)	25.17
	2.0 M	17.12 (1.07)	9.61 (0.99)	43.86	14.37 (3.84)	8.38 (3.49)	41.71
Dark jarrah	0 (Control)	6.67 (1.89)	5.95 (3.62)	10.75	6.67 (1.89)	5.95 (3.62)	10.75
	0.5 M	12.81 (3.24)	12.73 (0.30)	0.70	12.72 (1.93)	10.30 (2.97)	19.01
	1.0 M	16.16 (2.43)	11.71 (0.56)	27.54	13.99 (2.60)	10.12 (2.20)	27.67
	2.0 M	15.81 (1.73)	11.73 (0.48)	25.80	14.95 (3.25)	11.54 (1.38)	22.78

Surface activation using lithium and sodium hydroxides significantly improved shear strength of the glued laminates in both dry and wet conditions. There are several factors which may account for such improvements. Firstly, increased alkalinity of the treated wood surfaces could have provided favourable curing condition for the resorcinolic resins (Subramanian 1984). Secondly, the ability of hydroxides to cleave intermolecular hydrogen bonds in cellulose could enhance the bonding between wood and adhesive thus imparting high dry bond strength (Young *et al.* 1985). SEM observation on glueline structure of the untreated and treated laminates showed that adhesive penetration in the treated laminates was markedly deeper than in the untreated laminates (Balfas & Heady, unpublished data). This observation also revealed a different adhesive penetration between wood type, *i.e.*, it was greater in the treated karri than in the treated jarrah, but there was no clear difference in adhesive penetration with the application of different hydroxides and the different concentrations. The deeper adhesive penetration could bulk more wood fibres adjacent to the glueline, making them more water resistant and dimensionally stable, thus reducing the development of shear forces in the glueline on immersion. This effect may be responsible for the increased wet bond strength of the treated laminates.

Bond strength improvements in the treated laminates varied according to wood type, chemical and its concentration. The dry shear strength increased to a higher degree in jarrah than in karri (Table 3). For example, light and dark jarrah laminates treated with 0.5 M LiOH increased in dry shear strength by more than 110 and 92% respectively compared to the untreated specimens, whereas the karri laminates treated in this manner increased by less than 20%. This disparity might again be related to the different extractives contents between karri and jarrah. Wood extractives are considered as an important surface contaminant (*e.g.*, Hancock 1963, Chen 1970, Plomley *et al.* 1976, Young *et al.* 1986); hence it is possible that the greater amount of extractives in jarrah than in karri (Table 1) could contaminate the wood surface more severely. Hence, removal of extractives from wood surface by lithium and sodium hydroxides gave a greater effect on jarrah. Moreover, the treated jarrah laminates had higher wet shear strength than the treated karri. As discussed earlier with the untreated specimens, this variation is due to the higher dimensional stability of jarrah laminates.

In all cases, the LiOH treated laminates had higher dry and wet bond strengths than the NaOH treated laminates (Table 3). The precise reason for this is not known, but it could be due to the greater ability of LiOH in enhancing curing of the adhesive than NaOH (Subramanian 1984). The dry shear strength generally increased with increasing chemical concentration. However, improvement in wet shear strength mostly decreased with increasing concentration of the two hydroxides. The higher concentrations may increase the ability of chemical in removing extractives and other inactivating agents from wood surface, and may promote the formation of hydrogen bonding. This mechanism imparts high dry bond strength but no water resistance (Young *et al.* 1985).

It is clear from Table 3 that the use of LiOH at low concentration (0.5 M) could effectively resist the strength losses of karri and jarrah laminates during immersion. Whereas the application of 0.5 M solution of NaOH reduced the strength loss of karri, it increased that of jarrah laminates. The more effective protection of strength loss in karri might be related to the deeper adhesive penetration in its laminates as mentioned earlier, but the reason for the different ability between lithium and sodium hydroxides in preventing strength losses is not known. Results here suggest that surface activation using 0.5 M solution of LiOH is the most suitable treatment for improving the resistance of glued joint against dimensional changes in regrowth karri and jarrah laminates.

Although results from this study show that surface activation using lithium and sodium hydroxides simultaneously increased wettability and shear strength of the treated laminates, there was no clear relationship between wettability and shear strength either for the treated or untreated laminates (Figures 4, 5 and 6). This confirms the finding of Chen (1970) who found no correlation between bond strength and wettability in eight tropical species when using resorcinol formaldehyde as the adhesive. Jordan and Wellons (1977) also observed that there was no direct relationship between wettability and gluability in dipterocarp species using phenolic resins.

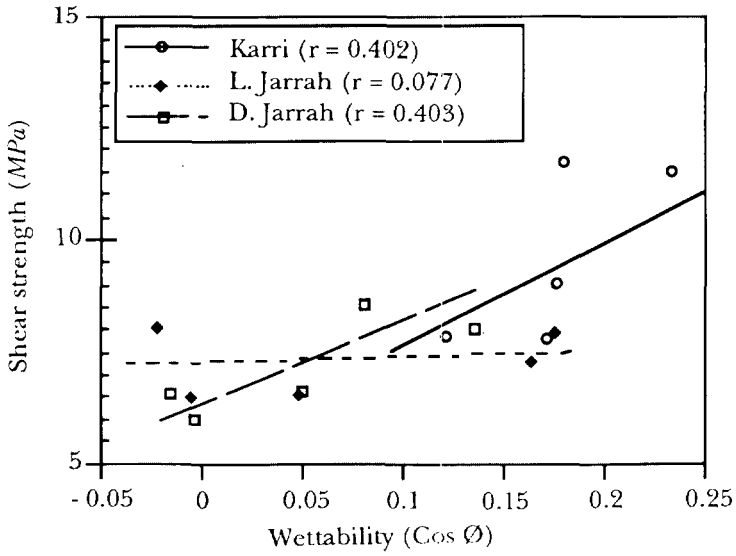


Figure 4. Relationship between wettability and shear strength of the controls

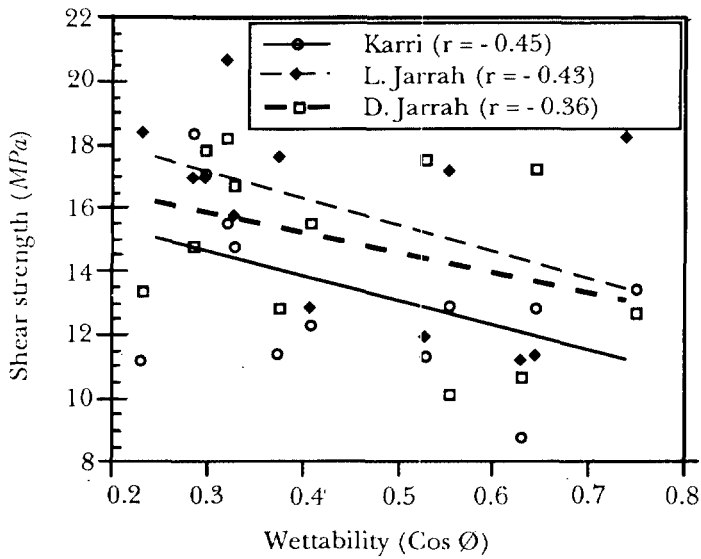


Figure 5. Relationship between wettability and shear strength of the LiOH treated samples

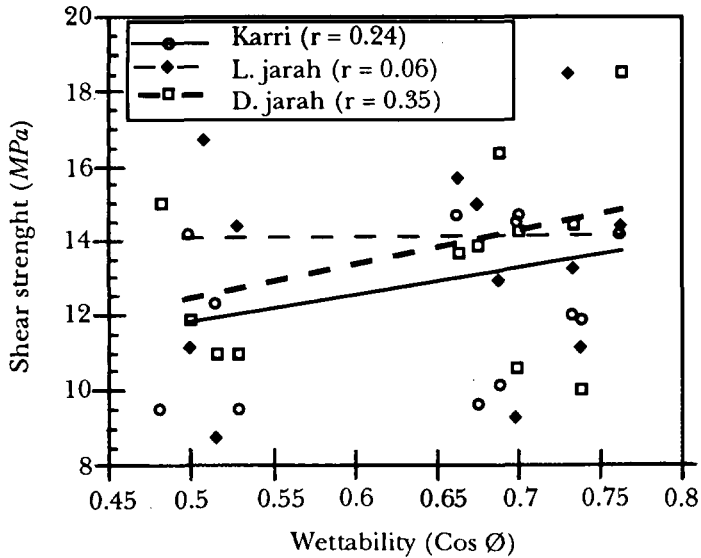


Figure 6. Relationship between wettability and shear strength of the NaOH treated samples

Conclusion

Adhesive bonding of regrowth karri and jarrah with resorcinol formaldehyde resin could be improved by surface activation treatment either using lithium hydroxide or sodium hydroxide. Treatment with lithium hydroxide gave higher improvements in the dry and wet bond strengths than treatment with sodium hydroxide. After treatment, the dry bond strength of jarrah laminates increased to a greater degree than that of karri. The untreated and treated jarrah specimens were significantly more resistant against wetting than the karri laminates. Application of higher chemical concentrations generally increased dry shear strength, but tended to reduce wet shear strength of the treated laminates. There was no linear relationship between wettability and shear strength for both the untreated and treated laminates.

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