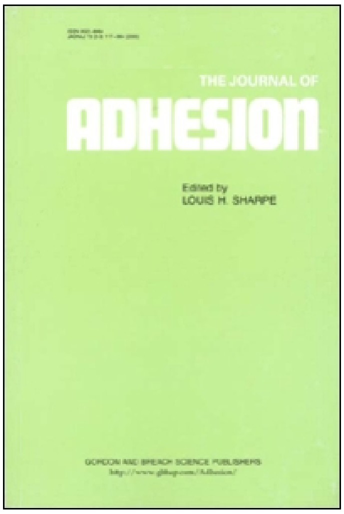

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The Improvement of Bond Strength Properties and Surface Characteristics of Resinous Woods*

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Apitong (*Dipterocarpus* spp.) and Caribbean pine (*Pinus caribaea Morelet*) contain high amounts of extractives that contribute to poor bonding. To reduce, if not to eliminate, the effects of these extraneous substances, surfaces of small wood blocks were Soxhlet-extracted for 8 hours by different solvents. Wettability of the wood surfaces was then measured by droplet and dynamic methods using water and dilute NaOH as liquids. Tensile shear strengths of extracted wood bonded with aqueous vinyl polymer isocyanate (API), resorcinol formaldehyde (RF) and polyvinyl acetate (PVAc) resin adhesives were also measured. Results revealed that although Caribbean pine had much higher resin content than Apitong, the former had better wettability than the latter. Solvent extraction of the adherend with either hexane or ethanol-benzene (1:2) for 8 hours was not enough to improve its wettability but enough to improve its gluability. However, successive extraction with hexane, methanol and ethanol benzene rendered the wood satisfactorily wettable. Generally, a direct relationship between wettability and bond strength could not be observed. In a separate experiment to improve bonding strengths, test specimens were either overheated or autoclaved for 4 minutes at 125°C during the pressing period. Autoclave treatment was found to be useful in increasing the bond strengths of API, RF, PVAc and urea formaldehyde (UF)-bonded Apitong and Caribbean pine.

KEY WORDS: Solvent extraction of wood; wettability; static and dynamic contact angles; vinyl polymer isocyanate adhesive; resorcinol formaldehyde adhesive; poly(vinyl acetate) adhesive; urea formaldehyde adhesive; surface treatment of wood; lap shear bond strength; dry heating; autoclaving.

1. INTRODUCTION

It is known that bonding of wood containing a high amount of extractives is difficult and a number of tropical woods, including resinous Apitong (*Dipterocarpus* spp.) and Caribbean pine (*Pinus caribaea* Morelet) belong to this category. Besides simple removal of extractives by light planing and solvent extraction[1,2], chemical methods

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which include oxidative activation[3,4,5] and other chemical treatments[6,7,8], could be applied to improve bond strengths. In the investigation of the relationship between extractives and gluability, the wettability study is of prime importance. It was reported that the relationship between wettabilities and strengths of adhesion joints glued with urea formaldehyde resin indicated a positive linear correlation[9]. This was not the case with phenol formaldehyde. Also, a lack of wettability of dry veneer at room temperature was not sufficient to predict its bondability. However, in the experiments by Wellons (1980)[10], the bonds of every dry wood, initially found to have good wettability, had inferior quality. The wettability of wood surfaces by liquid or adhesive resins might be increased by several measures. Light planing or sanding are physical methods which can be applied for this purpose. The most popular method is by extraction with organic solvent[11]. The objective of this study is to determine the wettability of resinous Apitong and Caribbean pine and to relate it to their gluing properties using different adhesives. The wettability after different surface treatments was also examined.

On the improvement of bond strengths of these woods, early investigators of the manufacture of particleboard suggested the advantages of heating with steam treatment before[12] and after[13] pressing. The other purpose of the study is to improve gluability of Apitong and Caribbean pine in a different approach or without pretreatment of the adherend. That is, treatment is done after spreading the adhesive and the adherends are put together. In this section, oven heating and autoclave treatments were applied at the start of pressing as measures to increase bond strengths.

2. MATERIALS AND METHODS

2.1. Surface Treatments for Apitong and Caribbean Pine

Wood blocks of size similar to that used in the preparation of the shear strength test specimens were subjected to the following treatments.

Scraping of wood surface Scraping was done by using a sharp blade at a right angle with the wood plane, moving it with slight sideboard pressure along the wood grain for about 10 times.

Wiping with hexane This was done by applying hexane to a piece of cloth and wiping the surface of the wood with a slight pressure for about 10 times.

Solvent extraction Extraction was done for 8 hours by the Soxhlet method.

2.2. Measurement of Contact Angles

Droplet method Using distilled water (pH 7) and dilute aq. NaOH (pH 11) as liquids, droplets (about 10 µl) were applied to the surface of the wood of a size similar to those used in strength test. A macro-photograph of the doplet using slide film was taken at different time intervals. The processed slide film was projected onto a projection screen and the contact angles were measured to the nearest whole degree using a protractor.

Dynamic method The advancing and receding contact angles between wood and water at 25°C were measured using a WET 6000 (RHESCA Co, Ltd.) dynamic wettability testing machine.

2.3. Measurement of Tensile Shear Strength of Solvent-Extracted Apitong and Caribbean Pine

Test specimens were prepared and tensile shear strengths were measured by the following method. Wood samples were cut into 80 mm (L) × 15 mm (W) × 5 mm (T) blocks and conditioned in a humidity- and temperature-controlled room to bring down the moisture content to 8–11%. Single-lap shear test specimens were prepared from the unplaned and unsanded sawn blocks by applying aqueous vinyl polymer solution isocyanate (API:PI Bond PI-127, Oshika Co.), resorcinol formaldehyde (RF: Oshika Resin D-33, Oshika Co.) and polyvinyl acetate emulsion (PVAc: Bond CH-18, Konishi Co.) adhesives into an area of 15 mm × 20 mm surface of both blocks using a metal spatula (Fig. 1). The gluing conditions as recommended by adhesive manufacturers are shown in Table I. Specimens were assembled and clamped using an ordinary double clip which can deliver about 5 kg/cm^2 on the glued portion. Clamping time for each adhesive was equivalent to the recommended pressing time. Test specimens were conditioned at 20°C and 65% RH for 7 days and tested under the same condition using a universal testing machine (Shimadzu Autograph AG 5000).

2.4. Dry Heating and Autoclave Treatments of Apitong and Caribbean Pine

Immediately after the start of clamping, sets of shear test specimens were heated in a laboratory oven at 125°C and for 4 minutes. Specimens were then cooled to room temperature and conditioned and tested as above. Another set of specimens were autoclaved at 125°C and pressure of 2 kg/cm^2 for 4 minutes, cooled, conditioned and tested.

3. RESULTS AND DISCUSSION

3.3. Contact Angles Measured by Droplet Method

Change of Contact angle with time. Within 10 minutes, the contact angle of distilled water on Apitong did not change much (87° to 75 °, a decrease of about 14% (Fig. 2)).

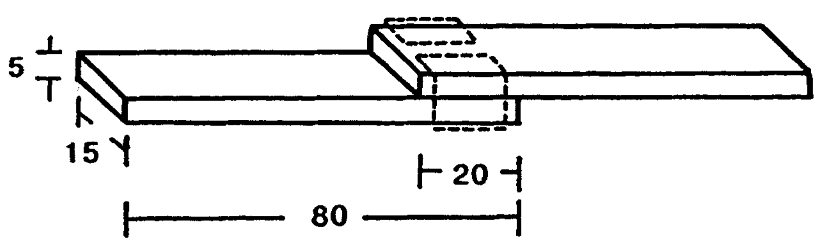

FIGURE 1 Single lap joint test specimen (all dimensions in mm).

Table I
Bonding conditions recommended by the adhesive manufacturers.

Adhesive	Name	R:H:F* Ratio (by weight)	Spread (gm^{-2})	Pressing time (h)	Pressing pressure ($kg\ cm^{-2}$)	Pressing temp. (°C)
RF	D-33	100:15:10	250	24	10	20
API	PI-127	100:15:5	250	2	10	20
PVAc	CH-18	100:0:0	222	20	2.2	20

*-R = resin, H = hardener, F = filler

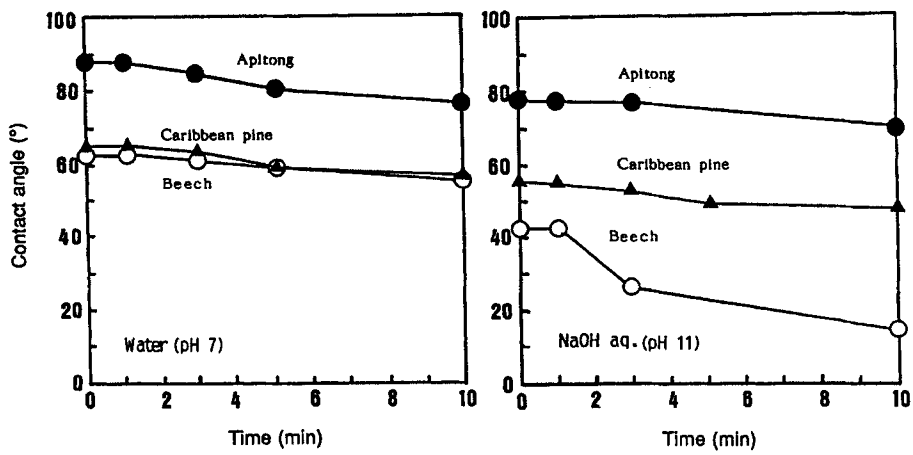

FIGURE 2 Changes of contact angles with time between liquid and wood.

The extent of the decrease in contact angle was the same for beech (*Fagus crenata* Bl.), a species low in extractives and Caribbean pine, where the contact angle dropped from about 65 to 55 degrees. There was about 20 degrees difference between contact angles of water (immediately after dropping the liquid) in Apitong and beech/Caribbean pine.

On the other hand, using aq. NaOH as the liquid, the values of contact angles for beech were lower than those for Caribbean pine, indicating advancement of wetting after 10 minutes.

Contact angles of different woods The values of contact angles for solvent-extracted Apitong, Caribbean pine and extractive-coated beech are shown in Table II. The pH of dilute aqueous NaOH (pH 11) approximates that of the commonly-used phenolic adhesives. Although the trend is similar, the values of contact angle for dilute NaOH solution were generally lower than that of distilled water (pH 7). For Apitong, the difference amounted to about 10 degrees. It is important to note that the contact angles of solvent-extracted Apitong and Caribbean pine are generally slightly higher that of the control. This indicates that although extraction removed some amount of extractives from the surface of the wood, it is still not effective in improving wettability. A possible explanation for this is that during extraction, the solvent has

Table II
Average contact angles between sessile drops of liquids and wood at 20°C

Wood	Contact angles, degrees	
	Distilled water (pH 7)	aq. NaOH (pH 11)
Non-resinous Apitong	70	70
Apiotng	87	78
Apitong extracted with hexane*	96	76
Apitong extracted with ethanol-benzene*	92	83
Caribbean pine	64	60
C. pine extracted with hexane*	71	60
C. pine extracted with ethanol-benzene*	73	62
Beech	62	43
Beech coated with hexane extractives**	85	78

* - Wood extracted for 8 hours by Soxhlet extraction method
**-Extractives added at 0.3 g/150 cm^2

penetrated deep into the wood and immediately after the extraction operation, the solvent inside, which contains a certain amount of dissolved extracts, moved outward together with the extractives. Upon reaching the surface, the solvent evaporates leaving behind the freshly exposed non-volatile extracts on the surface.

Table II also shows that there are relatively low contact angles of both liquids on Caribbean pine compared with Apitong although the latter has much lower extractives content. The difference was about 20 degrees. Also, the difference between the of Caribbean pine and beeach may partly explain the big difference in the value of bond strength for these woods. As mentioned above, for beech, the difference between the contact angles of water and NaOH solution is very much pronounced. The table also shows that in the absence of a large amount of extractives, the contact angles of liquid or adhesive at this pH changes more rapidly. For beech coated with extractives, the values of contact angles of both liquids approximated that of Apitong (control).

Most extractives are hydrophobic, that is, they prevent access of liquids into the wood itself. It is clearly shown that the presence of hexane extractives on the surface of wood is a big factor in its gluability. For Caribbean pine, the difference between contact angles of water and dilute NaOH solution was not significant. However, for the extracted Caribbean pine, a slight difference was observed.

3.2. Contact Angles Measured by Dynamic Methods

Table III shows the much higher contact angle of water or resinous Apitong compared with that on the non-resinous one. The advancing contact angles of extracted Apitong were even higher than for the control resinous Apitong. This agreed with

Table III

Average contact angles between water and wood at 25°C

	Advancing contact angle, degrees	Receding contact angle, degrees
Non-resinous Apitong	100.6	20.0
Apitong	117.5	33.1
Apitong extracted with hexane*	141.5	28.4
Apitong extracted with ethanol-benzene*	141.5	28.4
Caribbean pine	95.8	21.7
C. pine extracted with hexane*	100.1	17.7
Beech	85.0	35.5
Beech coated with hexane extractives**	99.8	40.6
Beech coated with diethyl ether extractives***	110.3	31.8

* -Wood extracted for 8 hours by Soxhlet extraction method
** -Extractives added at 0.3 g/150 cm^2

the data in the droplet method and confirmed the poorer wettability of wood after extraction. However, this is not so in the case of the values of receding contact angles which probably agreed with the "good wetting-good bonding" trend. The data also show the much lower advancing and receding contact angles for beech. It is interesting to note that the values of contact angles in the droplet method were much lower than those of the advancing contact angles and much higher than those of the receding contact angles.

When beech was coated with either hexane or diethyl ether extractives, the advancing contact angles naturally increased, especially in the case of the latter solvent, although this trend was not distinct in the case of receding contact angles. As in the previous method, the contact angles of water on extracted wood were slightly higher than those on the unextracted wood. However, for the receding contact angles, the trend was completely the reverse.

3.3. Relationship between Values of Contact Angles as Measured by Two Difierent Methods

Figure 3 shows the relationship between the values of contact angle determined by the two different methods. The lines describe the clear direct relationship between these values. As expected, most of the values of contact angle using dilute aqueous NaOH solution fell below the line because of lower the contact angles of the liquid in this pH range. Thus, it was found that one method serves as a good confirmative test for the trend of the measured values using the other method.

3.4. Contact Angles after Several Surface Treatments

In a different set of samples, wettability of both Apitong and Caribbean pine was measured after several surface treatments. The results are shown in Table IV. In

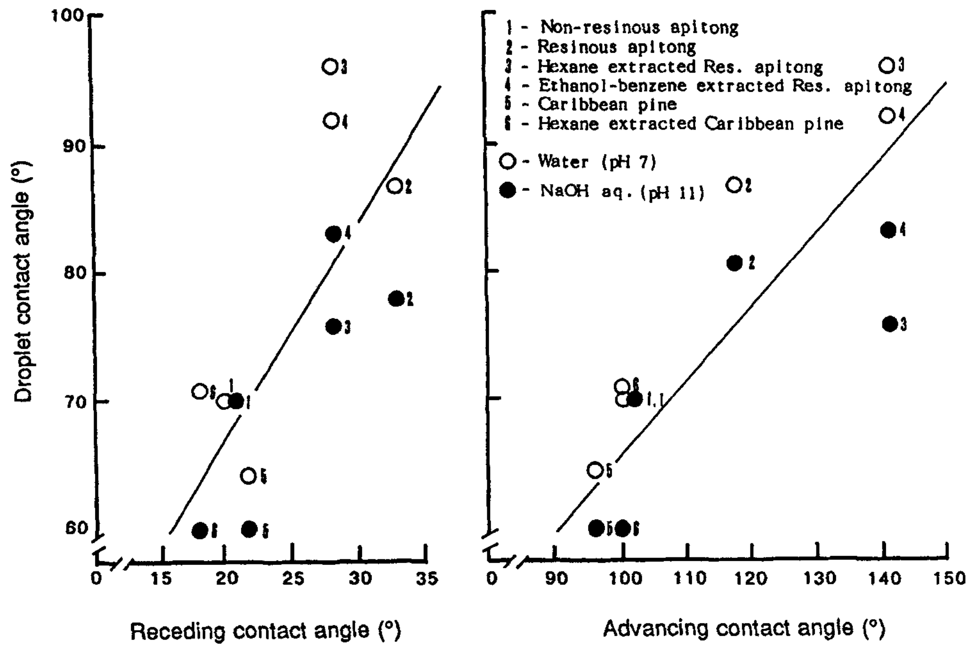

FIGURE 3 Relationships between values of contact angles measured by droplet and dynamic methods.

Table IV
Average contact angles (25°C) between sessile drop of liquid and wood after different treatments

	Contact angles*, degrees			
	Apitong		Caribbean pine	
	Water (pH 7)	aq. NaOH (pH 11)	Water (pH 7)	aq. NaOH (pH11)
Control	69	61	61	59
Freshly cut	55	55	60	64
Freshly scrapped	36	37	35	35
Freshly wiped	35	30	61	63
Successive extraction**	43	41	37	34

* -Measurements made after 1 minute
** -Extraction with hexane, methanol and ethanol-benzene; measurements made after 1 week.

Apitong, immediately after cutting, the wettability was slightly better than that of the samples after a week of conditioning. Scraping of the wood surface appeared to cause a big decrease in measured contact angle due to the removal of extractives on the surface. Scraping made the measurement of contact angles unreliable because of the difficulty for the droplet to exist on a rough surface. Wiping with hexane resulted in a considerable inprovement of wetting. Wiping simply removed the extractives from the surface at a much lower temperature than that of Soxhlet extraction. This limited the possible movement of extractives into the surface caused by high temperature.

In the case of Caribbean pine it was noted that scraping of the surface brought about low values of contact angles. However, because of the nature of its extractives (hard resin), scraping just exposed another layer of this wood "embedded" in resin. Thus, low values of contact angles can be attributed to the change in the roughness of the surface. This was also true in the case of contact angles measured immediately after cutting. Similarly, wiping with hexane could not dissolve and remove any considerable amount of the resin, resulting in insignificant change in the values of contact angles.

Successive extraction of both woods increased wettability as shown by the decrease of measured contact angles. This indicated that successive extraction was enough to remove a considerable amount of extractives from the surface, or from the inside of the wood near the surface, making it more wettable even after one week. Also, by using this procedure, there were more kinds of extractives removed than by using only a one stage extraction by a single solvent.

3.5. Relationship between Wettabilities and Tensile Shear Strengths

Results (Fig.4) revealed that woods which contain relatively high amounts of extractives and exhibit inferior wettability (higher values of contact angles) have poor bond strength. Results also showed that after solvent extraction the bond strength of API-bonded Apitong increased slightly while that of RF-bonded Apitong increased moderately. For Caribbean pine, using any of the adhesives, the bond strengths were improved by solvent extraction of the adherend. After solvent extraction, there were no significant changes of droplet contact angles on both Apitong and Caribbean pine but the dynamic contact angles increased. This means that solvent extraction was not effective in increasing the wettability of wood though it may be advantageous in improving its gluability. It is believed that a small amount of extractives from the inner portions of wood migrate into the surface in a short period. The amount was enough to cause poor wettability but not enough to affect gluability seriously.

Figure 5 summarizes the relationship between the measured contact angles and tensile-shear strengths. The high values of bond strength for wood extracted with solvent were conspicuous. However, a direct relationship between the bond strengths and contact angles could not be observed. As was explained above, the extraction treatment removed some amounts of extractives from the inner portion of the wood. Thus, during bonding, the adhesive could penetrate the wood relatively more easily.

3.6. Bond Strengths of Apitong after Dry Heating and Autoclave Treatments

The effect of oven-heating and autoclave treatments on bond strengths of resinous Apitong are described in Fig. 6. After autoclave treatment, bond strengths increased for all types of adhesives. On the other hand, oven heating improved only the bond

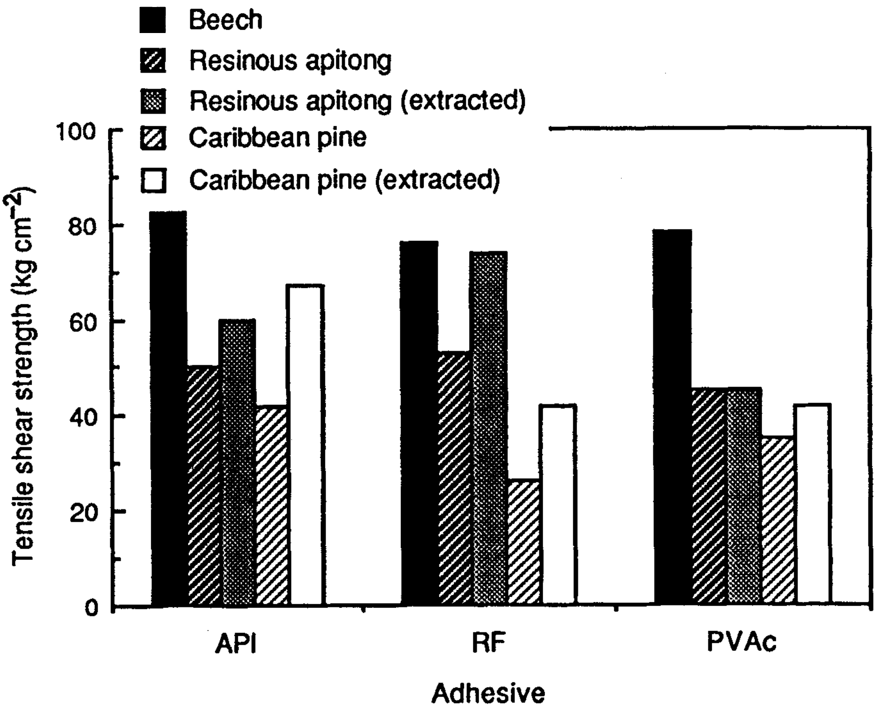

FIGURE 4 Tensile shear strengths of bonded Apitong and Caribbean pine.

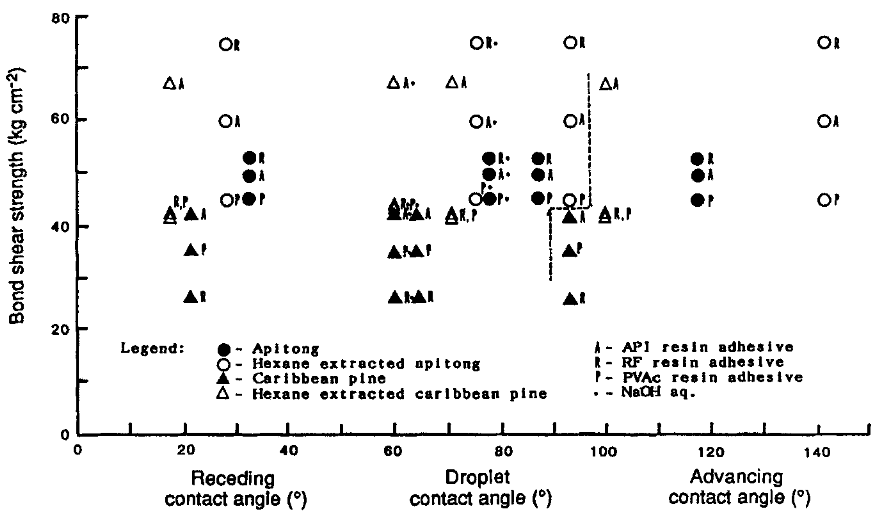

FIGURE 5 Relationships between the measured contact angles and bond strengths.

strength of RF-bonded Apitong, increasing it by about 20%. Autoclaving increased the bond strengths of Apitong bonded with API, PVAc and UF by 65, 170 and 70%, respectively. However, for the latter two adhesives, the resulting strengths were still about half of the strength for API and RF bonded wood. It is interesting to note

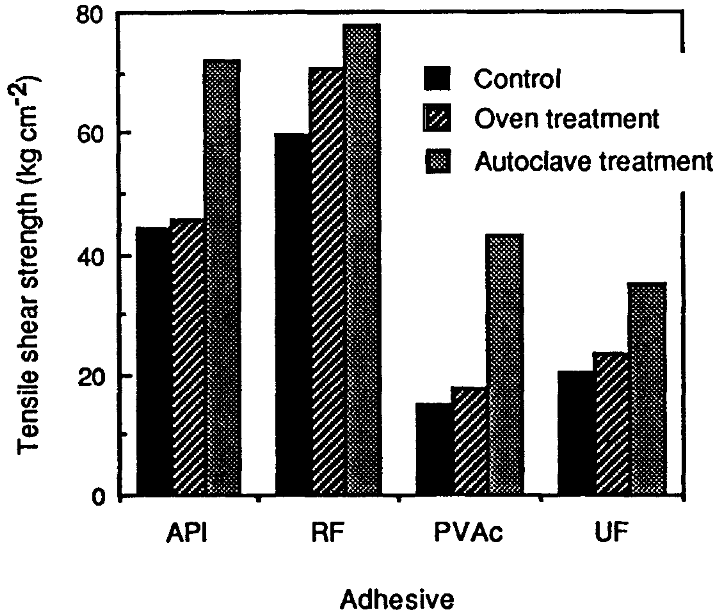

FIGURE 6 Effect of oven and autoclave treatments at pressing on shear strengths of bonded Apitong.

that the biggest improvement was observed for the adhesive which originally bonded Apitong the poorest (PVAc), and the least improvement for the adhesive which performed well (RF).

Without autoclave treatment, the values of bond strength for API and RF widely differed but, after autoclaving, the bond strengths of specimens bonded with API were comparable with those of RF. The bond strengths of PVAc- and UF-bonded and then autoclaved specimens were only similar to those of specimens bonded with API without autoclaving.

The corresponding wood failures after strength test of autoclaved Apitong are shown in Figure 7. A very remarkable increase was observed in API- and RF-bonded specimens. This observation is an indication of improved penetration of adhesives. However, for PVAc and UF adhesives, although bond strengths had improved after autoclave treatment, wood failure did not increase. The reason for this is unclear.

3.7. Bond Strengths of Caribbean Pine After Dry Heating and Autoclave Treatments

The effects of oven heating and autoclave treatments on the bond strengths of Caribbean pine bonded with different adhesives are shown in Figure 8. In all cases, both heating and autoclaving brought about increases in the values of lap-shear strength compared with the control, with autoclaved test specimens showing higher values than those of the dry-heated specimens. The trend is obvious in the case of RF and UF. In the case of RF, lap-shear strength increased from 23 to 56 kg/cm^2 (or an increase of about 120%). Moderate increases of about 40% and 30% in lap-shear strength were observed for wood bonded with API and PVAc,

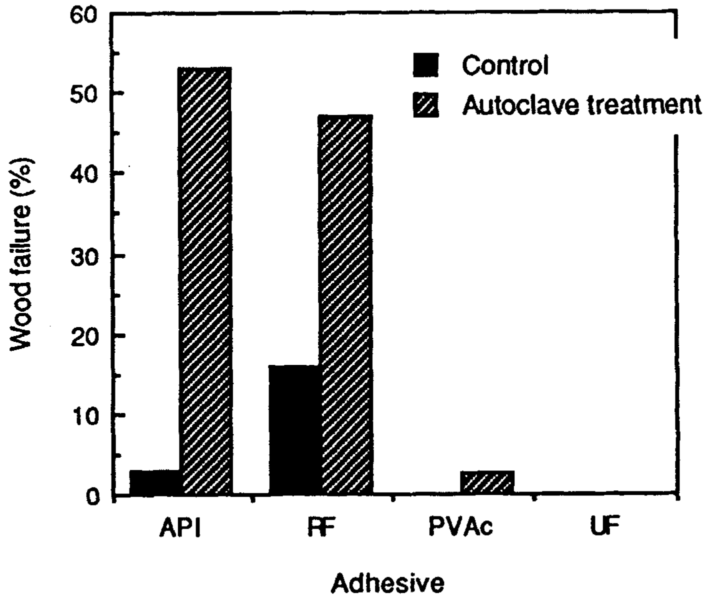

FIGURE 7 Wood failure after tensile shear strength test of resinuous Apitong bonded with different adhesives and with autoclave treatment.

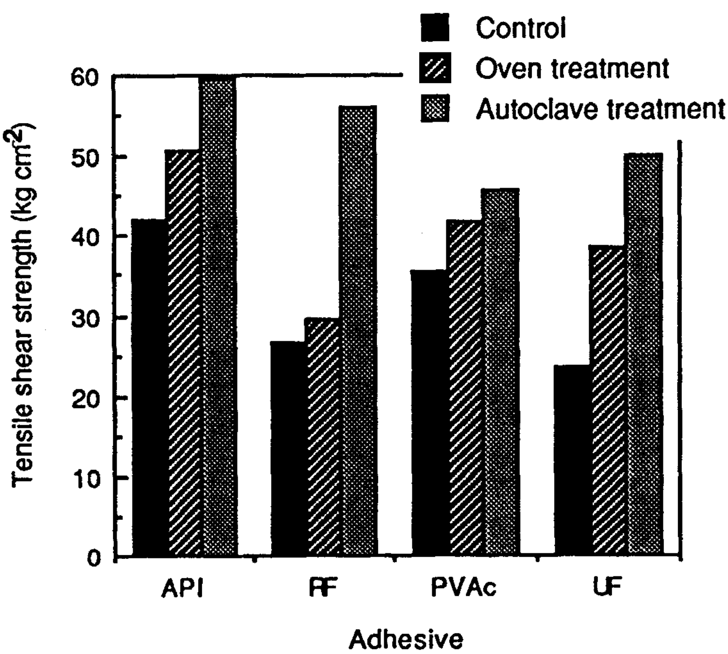

FIGURE 8 The effect of oven and autoclave treatments on the tensile shear strengths of Caribbean pine bonded with different adhesives.

respectively. It could be observed that, as in the case of Apitong, the improvement of bond strength was large when the value of the control was relatively low, that is, in the case of RF and UF.

It was clearly shown that, without any treatment, API-bonded Carribbean pine gave the highest lap-shear strength values while UF-bonded wood had the lowest shear strengths. For API and RF, comparable values could be observed after autoclave treatment. The same trend is true for PVAc and UF. Heating was also effective in increasing the bond strengths of wood bonded with UF where the treatment resulted in an increase of about 65%. There was no difference in lap-shear strengths between the control and heated specimens bonded with RF.

In both Apitong and Caribbean pine, strength improvement was made possible. When the adhesive is heated, viscosity is reduced enabling it to flow and increase contact with the surfaces of the wood[14]. High temperature also leads to faster curing of crosslinking types of adhesives. Previous studies suggested that urea formaldehyde and isocyanate adhesives cure at temperatures just below 100°C[15]. It was also reported that at high temperature the extractives which exist as a layer tend to disperse into the adhesive, thus improving the adhesive-wood contact[16]. Moreover, investigations of the change of temperature near the glue-line during both treatments indicated that, at similar exposure temperature, autoclaving increased the temperature near the glue-line to a value higher than that when specimens are dry heated. That is, the difference of the extent of bond improvements between oven and autoclaved-treated specimens was due to the effectiveness of the latter treatment in bringing the temperature at the glue-line to a value higher than that of the former.

4. CONCLUSION

In the studies of wood wettability, it was shown that although Apitong contained a much lower concentration of extractives, its wettability was poorer than that of Caribbean pine. Solvent extraction of the adherend for 8 hours was not enough to increase the wettability of these woods but was enough to improve their gluability. However, successive extractions with different solvents rendered them satisfactorily wettable. When coated on beech, hexane extractives in particular caused poor wettability.

In an attempt to improve gluability, oven heating treatment at 125°C for 4 minutes during pressing did not cause significant improvement of bond strengths for Apitong but increased those of Caribbean pine. On the other hand, autoclave treatment at the same temperature and duration, and at a pressure of $2 kg/cm^2$, was found to be useful in increasing the bond strengths of API- and RF-bonded Apitong, and the Caribbean pine bonded with API, RF, PVAc and UF adhesives.

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