Chapter 6
Penetration of Liquid Phenol Formaldehyde and Polymeric Diphenylmethane Diisocyanate Adhesive into Calcutta Bamboo

6.1 Introduction

Penetration of adhesive into the coarse capillary structure of wood is possible when a good wetting condition is achieved [1]. Creation of a bond between an adhesive and the wood substrate requires adequate interpenetration of the resin and wood components, and the development of links between the resin and the exposed wood surface [2]. The mechanism of the link between the resin and wood components, which is still being debated today, generally is thought to involve mechanical interlocking, covalent bonding, and secondary interaction, such as the Van der Waals forces and the hydrogen bonds [1,3]. Penetration of the adhesive promotes all of these mechanisms. Molecular weight, pH and temperature of the adhesive, and the moisture content, density and permeability of the substrate, will affect the penetration. Flow properties of the water component are responsible for the fluidity of the adhesive. Other variables, such as the material characteristics, processing factors, and methods of heating the adhesive bond, will also influence adhesive penetration [4]. Direction of penetration, permeability, porosity, roughness, surface energy, temperature, pressure, and time are among the other wood and processing factors that could influence the adhesive penetration [1, 5, 6]. In the case of bamboo, many researchers investigated the anatomical variability of bamboo in relation to orthogonal direction, between internodes and nodes, as well as location along the length of the culm. These variables in bamboo may influence the adhesive penetration and were investigated in this study.

Adhesive penetration definition by Sernek et al [4] is the spatial distance from the interface of the adjoining substrate. As defined by Brady and Kamke [7], the volume containing the wood cells and adhesive is the interphase region of the adhesive bond. The depth of penetration of the adhesive determines the size of the interphase region. According to Johnson and Kamke [8], excessive penetration will result in starved bondlines. Conversely, insufficient penetration will leave a thick film of adhesive on the surface and limited surface contact with the interior surfaces for chemical bonding or mechanical interlocking. An ideal amount of adhesive penetration would repair machining damage to the wood surface and permit better stress transfer between laminates.

The main objective of this study was to measure the effective penetration into Calcutta bamboo at different levels of moisture content and to evaluate the effect of direction and section in the culm.

6.2 Experimental

6.2.1 Materials

Calcutta bamboo culms described in previous chapter were also used in the penetration analysis. Upon arrival, the culms were cut into 4 ft. long segments, and were placed in a conditioning chamber for several weeks. Moisture content was monitored until equilibrium was reached (Temperature = 20^{o}C and Relative Humidity = 65%). Two types of adhesives were used in this study, phenol formaldehyde (PF) and polymeric diphenylmethane diisocyanate (pMDI). PF resin obtained from two sources. A liquid PF for parallel strand lumber (PSL) was obtained from Georgia Pacific Resins, Inc., a liquid PF for the core layer of oriented strand lumber (OSB) was obtained from Neste Resins, and pMDI for OSB was obtained from Huntsman Polyurethanes. The viscosity of PF-PSL, PF-OSB and pMDI at $25^oC \pm 0.5^oC$ were 2200 cps, 190 cps and 300 cps respectively.

6.2.2 Methods

Specimens for this experiment were taken from the culm according to Figure 3.1 in chapter 3. The bamboo culms were cut and sampled in the same manner described in previous chapters. Specimens were taken from locations 1 and 2 for all the penetration analysis. Specimens at different sections (nodes) and directions (radial and tangential) were also taken from the same locations for the comparison study. Measurements were made on the fresh surface of a specimen with thickness ranging from 2 mm to 5 mm. The different thickness was due to the different thickness of the culm wall. The length and width were approximately 2.5 cm by 1.2 cm. All the specimens were conditioned at 20^oC with 65% RH, except for the study on the different level of moisture content. The fresh surface was obtained by using 220-grid sandpaper, followed by a wash of compressed air before the adhesive was applied to the surface. All surfaces were sanded at the same rate and tested within a 2 hour period. A five-microliter pipet was used to manually apply the drops of adhesive.

Specimens for the different moisture content levels were taken from the bottom portion of the culm. All specimens were cut from adjacent sections to minimize bias. Two methods of conditioning were used, namely by means of saturated salt solution or a force-air conditioning chamber. Twenty specimens were exposed to each of six different moisture content conditions. Three conditions utilized saturated salt solutions (Lithium chloride, calcium chloride and sodium dichromate) and the other three utilized the conditioning chamber. Table 3.2 in Chapter 3 lists the saturated salt solutions and the conditioning (relative humidity and temperature) control used in this study. In addition, specimens conditioned at 20^{o}C with 65% RH were also used. The six environments yielded equilibrium moisture contents of approximately 4, 6.5, 7.5, 9.5, 12 and 19%. The apparatus and procedure of conditioning followed the standard guide for moisture conditioning of wood and wood-based materials, ASTM D 4933-91 [9]. The apparatus used and the preparation of the saturated salt solutions followed the standard practice for maintaining constant relative humidity by means of aqueous solution, ASTM E 104-85 [10]. Specimens for comparison of nodes and internodes, as well as for the radial and tangential directions, were conditioned at 20^{o}C with 65% RH to achieve a moisture content of approximately 12%.

After the desired moisture content was achieved, adhesive drops were applied to the specimens. At least two 0.5 μl drops of liquid PF-PSL and pMDI adhesive were placed along the length of the specimens that were used for the different moisture levels. One or two drops of liquid PF-OSB were placed on the specimens representing nodes and internodes, and radial and tangential directions.

At least 30 drops of liquid adhesive were used in the analysis. The specimens were allowed an additional ten-minute open-assembly and then heated in a convection oven at 103^{o}C overnight.

The specimens with the cured adhesive drops were cut across the drops with a small jigsaw, submerged in water, and were placed under a vacumm for 60 minutes. The specimens were then sliced on a microtome to produce transverse sections of 60 μm thickness, through the middle of the adhesive droplet. The thin sections were set in a 0.5% Toluidine Blue O solution for at least 15 minutes. The sections were then rinsed in distilled water, soaked in a 70% ethanol, and followed by a soak in 100% ethanol. The sections were then mounted on microscope slides using glycerin.

The microscope slides were observed using an epi-fluorescence microscope, 100 W mercury lamp, 5x objective lens, and a 515-nm emission and 470-nm excitation filter-set. The Toluidine Blue O suppressed the autofluorescene of the bamboo. Black and white images were captured using a video camera (Dage-MTI, CCD72, 0.0004fe sensitivity). The images were processed and analyzed using ImagePro Plus software (Media Cybernetics). Adhesive was observed in the cell lumens. Measurement were made of effective penetration (EP), average penetration (AP) and the maximum penetration (MP), as defined by Sernek et al [4] (Figure 6.1). The EP is the total area of adhesive detected in the interphase region of the bondline divided by the width of the bondline. The AP is the average distance of penetration of the three most distant adhesive objects detected. MP is the maximum distant penetration detected, measured at the maximum edge of the adhesive object. Adhesive objects in the image were thresholded manually to differentiate the bright adhesive objects from the darker bamboo background. The area of the highlighted objects and the maximum distance were then measured using the digital image processing and analysis software. The EP, AP and MP were calculated using Equations 6.1, 6.2 and 6.3 respectively.

$$EP = \sum_{i=1}^{n} A_i / x_o \tag{6.1}$$

where, A_i is the area of the ith adhesive object (μm^2), n is the number of objects and x_o is the width of the maximum rectangle defining the measurement area (1263μm).

$$AP = \sum_{i=1}^{3} (y_i)/3 \tag{6.2}$$

where y_i is the distance to the furthest edge of the three most distant adhesive objects from the surface. The average penetration is an addition to the formula used by Sernek et al [4]. They name this as MP instead of AP. Only three most distance objects were measured in this study compared to 5 most distance objects. This method was faster and appropriate, since the penetration is more uniform in Calcutta bamboo.

$$MP = y_{max} \tag{6.3}$$

where y_{max} is the furthest edge of the most distant adhesive object from the surface. MP calculation is different from the method used by Sernek at al [4]. This is appropriate since the structure for Calcutta bamboo is different from timber.

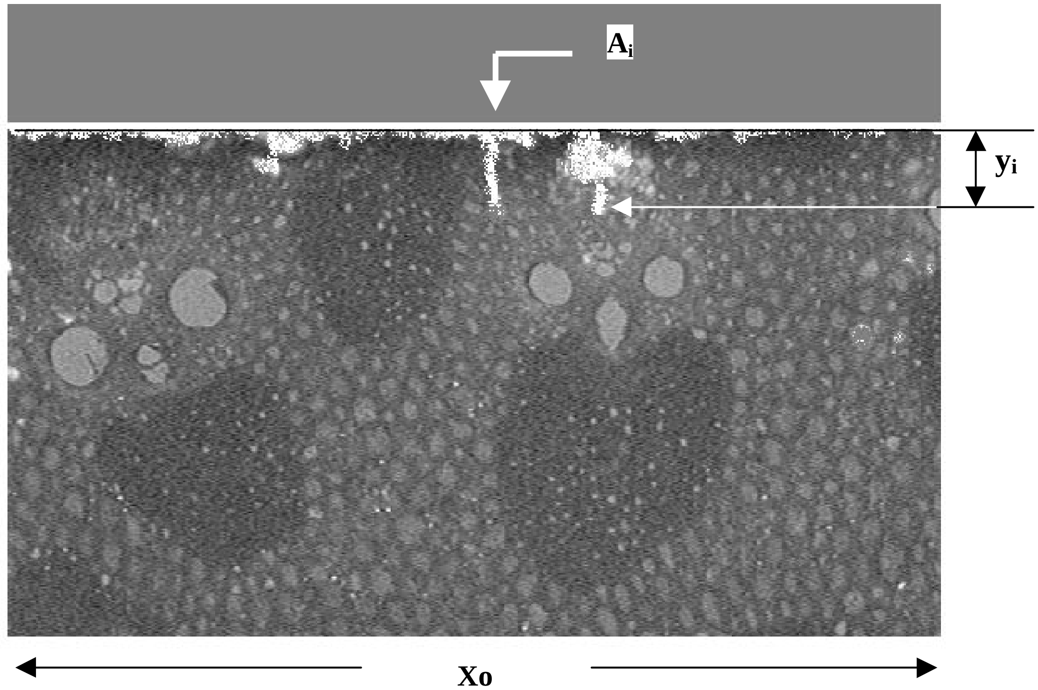


Figure 6.1. Graphical explanation of effective penetration, average penetration and maximum penetration. Illustration of penetration in the vascular bundles.

Multiple comparisons between the adhesive type, moisture level, nodes and internodes and between radial and tangential direction was carried out using the SAS statistical software package. Only the EP value was used in the comparison procedure for the different sections and directions.

Statistical Test

The model considered for the one-way analysis of variance is shown below:

$$y_{ij} = \mu + \alpha_i + \varepsilon_{ij} \qquad (3.5)$$

where:

y = observation (physical properties)
μ = mean
α = treatment (effect of different portion)
ε = error

One-way analysis of variance with post-hoc tests was performed on the adhesive penetration for the different moisture levels. The null hypothesis for the one-way ANOVA is shown below

H_o: $\alpha_1 = \alpha_2 = \alpha_3 = \alpha_t = 0$

H_a: At least one of the α differ from 0

The null hypothesis was that different moisture levels had the same mean adhesive penetration. If the H_o is true, then further tests do not need to be conducted. If H_o is not true, then the corresponding alternative hypothesis is H_a, at least one of the mean adhesive penetration differs from others. In this case the multiple comparison procedure, Tukey's studentized range (HSD) test was performed. The test procedure for comparing the adhesive penetration between nodes and internodes, and between radial and tangential directions was carried out using the two-sample t-test. The null hypothesis (H_o) was that the nodes and internodes, or radial and tangential directions have the same mean adhesive penetrtation

H_o: $\mu_1 = \mu_2$

H_a: $\mu_1 \neq \mu_2$

6.3 Results and Discussion

6.3.1 Effective Penetration of Adhesives on Calcutta Bamboo

The cured resole PF-PSL, PF-OSB and pMDI on transverse plane of Calcutta bamboo are shown in Figure 6.2, 6.3 and 6.4 respectively. Table 6.1 shows the analysis of variance of the effective penetration (EP) of the adhesives in Calcutta bamboo. Comparison was first done on the three adhesives types, PF-PSL, PF-OSB and pMDI. From Table 6.2, the mean EP of PF-PSL, PF-OSB and pMDI were 16.9μm, 15.0μm and 6.6μm respectively. Figure 6.5 illustrates the multiple comparisons seen on the three adhesive types using Tukey's studentized (HSD) test. The result showed that there was no significant difference in the effective penetration between the two PF adhesives, although their viscosity was different. The viscosity of PF-PSL was 2200 cps, while PF-OSB was 190 cps. The effective penetration of the two PF adhesives were, however, significantly different from the pMDI. The effective penetration of pMDI was very small compared to the two PF adhesives. This is true since in pMDI, more solids content was added compared to PF. The pMDI wets the interior surfaces better than PF and flows longitudinally. The PF tends to bulk up in the lumens and is therefore easier to be located (Figures 6.2 to 6.4).

Results shown in Table 6.1 also indicate that there was no significant difference of the effective penetration at different levels of moisture content for the PF-PSL and pMDI. The mean value of the effective penetration of PF-PSL and pMDI at different levels of moisture content is presented in Table 6.2. The moisture content had no significant statistical affect on the effective penetration of

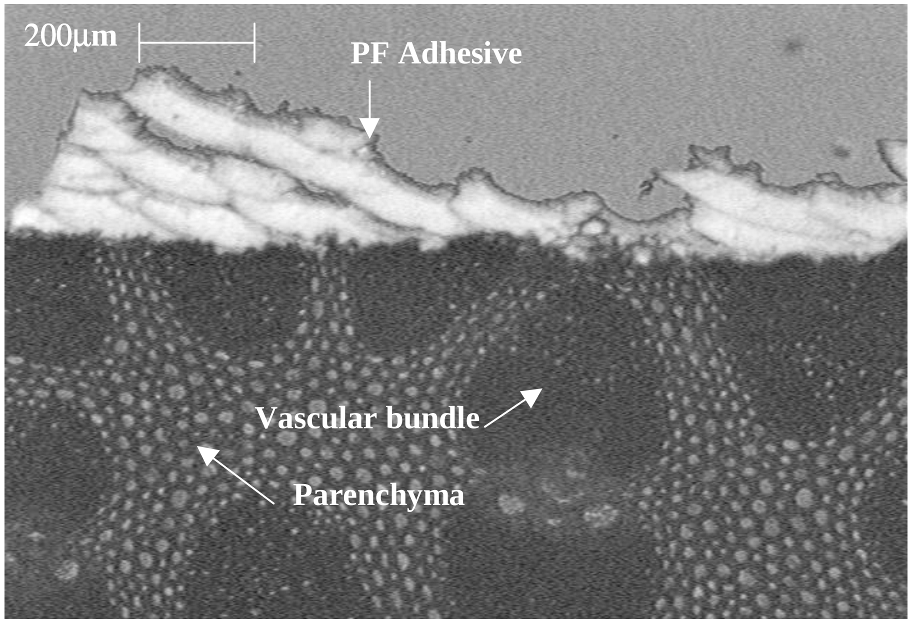


Figure 6.2. Cured resole PF-PSL adhesive on transverse plane of Calcutta bamboo.

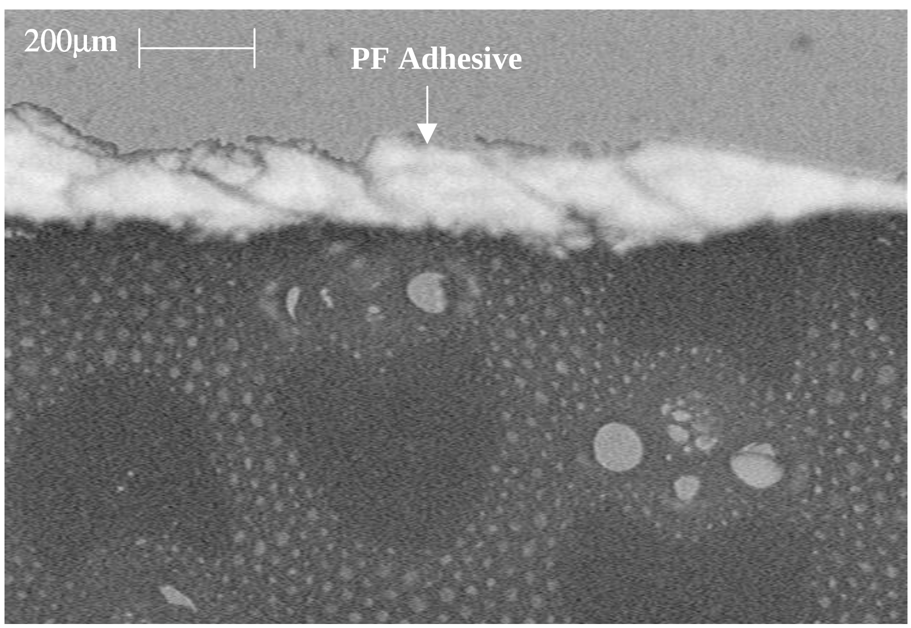


Figure 6.3. Cured resole PF-OSB adhesive on transverse plane of Calcutta bamboo.

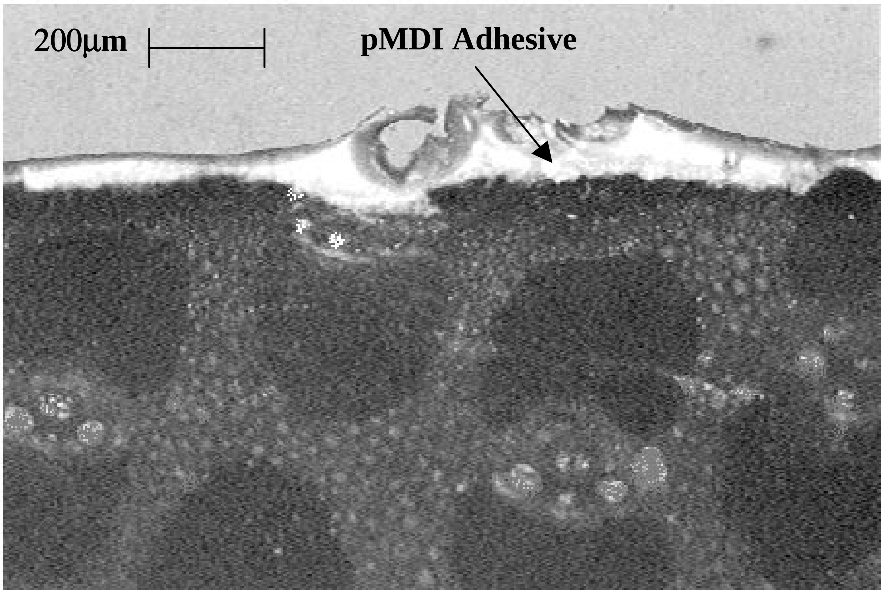


Figure 6.4. Cured resole pMDI adhesive on transverse plane of Calcutta bamboo.

Table 6.1. Analysis of variance of the effective penetration of *Dendrocalamus strictus* culms using PF and pMDI at different source of variation.

Source of variation	DF	Sum of Squares	Mean Square	F-value
Adhesive Type	2	1439.39	719.70	16.66(HS)
MC variation in PF[1]	4	564.33	141.08	2.89 (NS)
MC variation in pMDI	4	37.85	9.46	0.54(NS)
Direction[2]	1	4.56	4.56	0.13 (NS)
Section[3]	1	689.10	689.10	25.35(HS)

(HS) indicates significance at the 1% level of probability
(NS) indicates not significant
1-PF type is GP806D39 for PSL
2-Direction is associated with Radial and Tangential, PF type is OSB core
3-Section is associated with Internodes and Nodes, PF type is OSB core

Table 6.2. Mean effective penetration of adhesive (µm) of *Dendrocalamus strictus* culms using PF and pMDI at different source of variation

Adhesive type (at 12% MC)		
PF(PSL)	PF(OSB)	PMDI
16.88 (24.77)	14.96 (6.09)	6.57 (4.40))

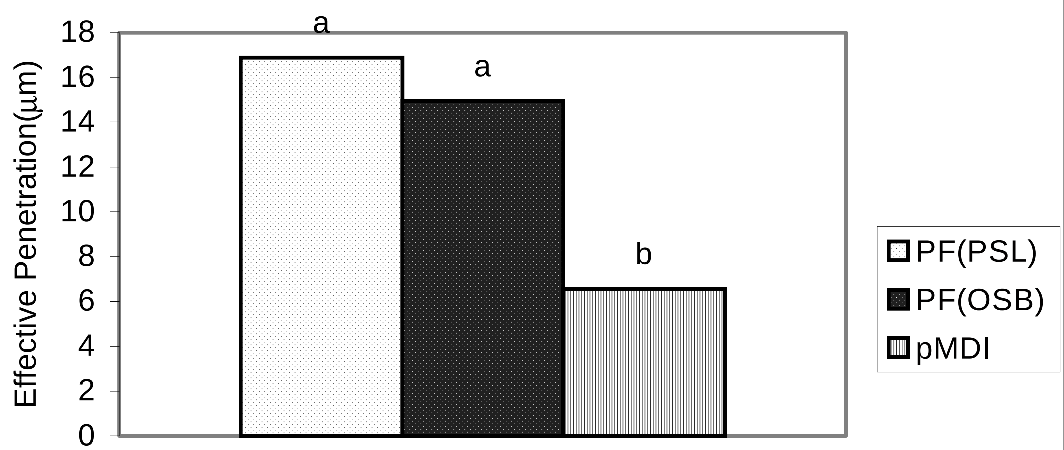
PF[1] at different MC level				
4.0%	6.5%	7.5%	9.5%	12.0%
15.50 (7.46)	17.88 (5.63)	20.55 (4.74)	20.37 (8.15)	16.88 (8.26)

pMDI at different MC level				
4.0%	6.5%	7.5%	9.5%	12.0%
4.98 (2.30)	6.40 (4.20)	6.51 (5.88)	6.56 (2.84)	6.57 (4.40)

Direction[2] (at 12% MC)	
Tangent	Radial
14.96 (6.09)	14.41 (5.91)

Section[3] (at 12% MC)	
Tangent	Radial
14.96 (6.06)	7.92 (3.95)

Number in parenthesis associate to standard deviation
1-PF type is GP806D39 for PSL
2-Direction is associated with radial and tangential, PF type is OSB core
3-Section is associated with internodes and nodes, PF type is OSB core
All penetration were measured at tangential direction except the penetration at radial direction.



Note:Means with the same letter are not significantly different at p<0.01 by Tukey's studentized range(HSD)test

Figure 6.5. Comparison of the effective penetration of *Dendrocalamus strictus* using PF(PSL), PF (OSB core) and pMDI adhesive. (Average moisture content for all specimens was 12%)

PF-PSL, and pMDI adhesives. Effective penetration is presented in Figures 6.6 and 6.7. In Figure 6.6, the effective penetration of PF-PSL adhesive starts at a lower value at 4% MC, increased at a higher value between 5 to 10% MC and decreased again after 10% MC.

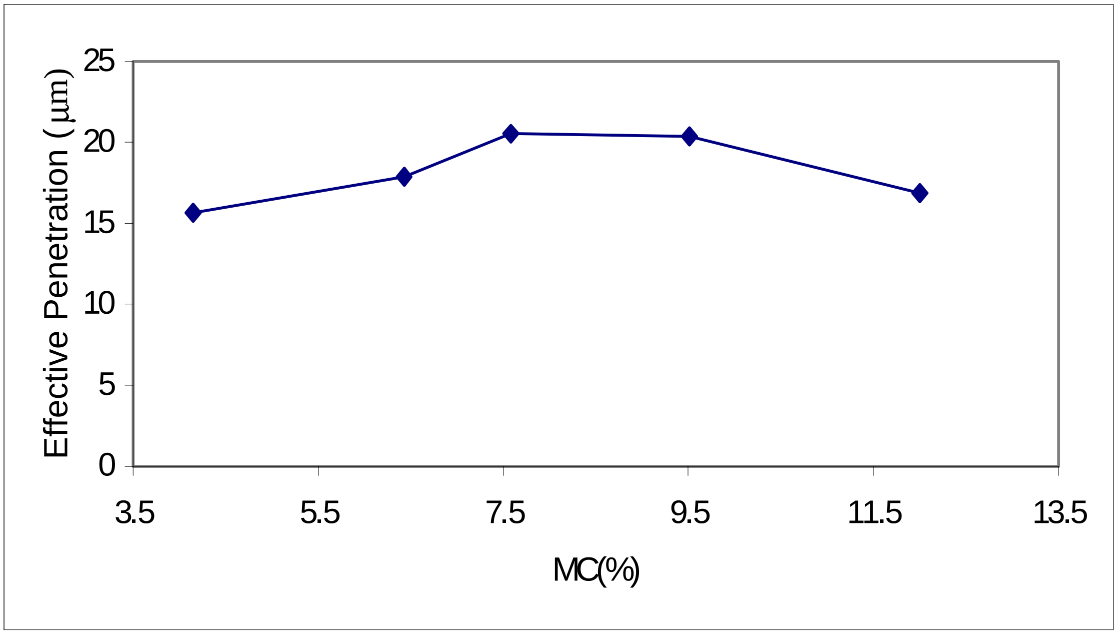


Figure 6.6. Effective penetration of PF adhesive versus moisture content of *Dendrocalamus strictus.*

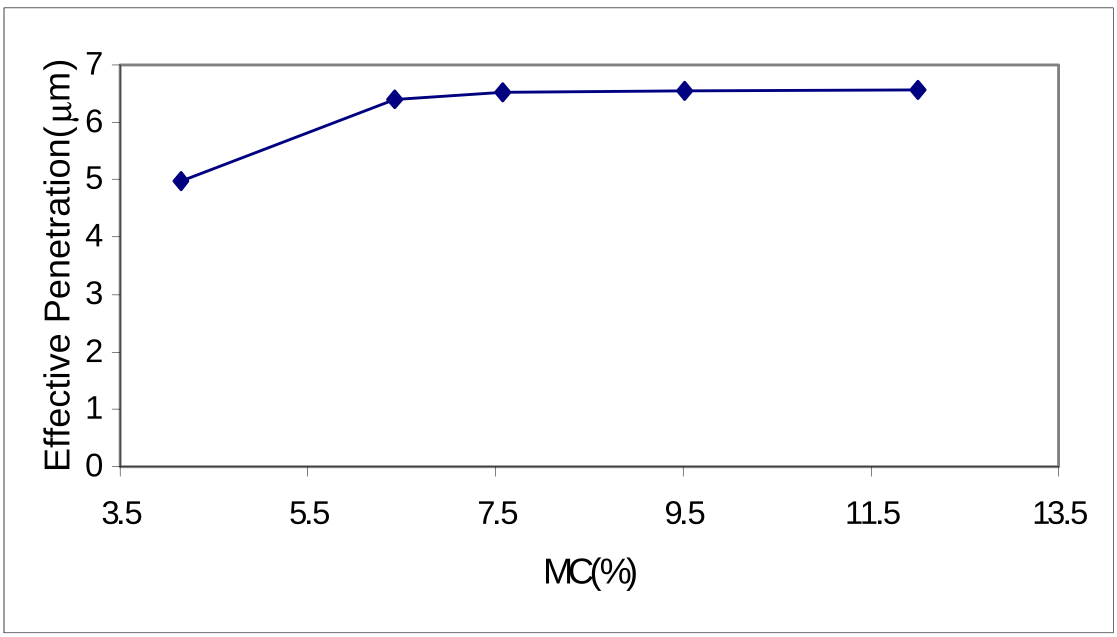
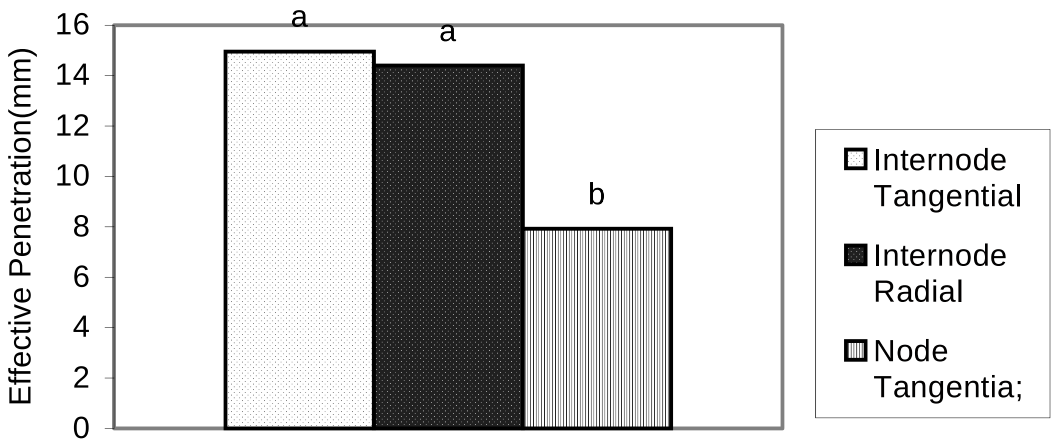


Figure 6.7. Effective penetration of pMDI adhesive versus moisture content of *Dendrocalamus strictus.*



Note:Means with the same letter are not significantly different at p<0.01 by Tukey's studentized range(HSD)test

Figure 6.8. Comparison of the effective penetration of *Dendrocalamus strictus* in different directions and sections using PF (OSB Core) type adhesive. (Average moisture content for all specimens was 12%)

Comparison was also made between the radial and tangential directions. The measurement was done on the internode sections using the PF-OSB resin. From Table 6.1 and from the graphical explanation in Figure 6.8, there was no significant difference of the effective penetration of PF resins between the radial and tangential directions. Due to the lack of radial transport in bamboo (rays), the adhesive penetrates equally in both directions. Average effective penetration of PF resins for radial and tangential (internodes) was 14.4 μm and 15.0 μm respectively.

The next comparison was performed on different sections of Calcutta bamboo namely the internodes and nodes. Effective penetration was measured using PF-OSB resins in the tangential direction. Measurements previously made in the tangential direction were again used to compare with the nodes. From Table 6.2, the effective penetration for internodes and nodes were 15.0 μm and 7.9 μm respectively. Statistical analysis showed that there was a significant difference between internodes and nodes (Table 6.1 and Figure 6.5).

6.3.2 Average and Maximum Penetration of Adhesives on Calcutta Bamboo

Average penetration (AP) and maximum penetration (MP) analysis of Calcutta bamboo was carried out using PF-PSL and pMDI adhesives. AP and MP were measured at different levels of moisture content. In this section, only the effect of moisture content on AP and MP, using PF-PSL and pMDI adhesive, were investigated.

Analysis of variance of AP and MP in Calcutta bamboo, using PF and pMDI, is shown in Table 6.3. There were no significant differences found in any of the moisture content levels for the AP and MP with either adhesive type. However, the mean value of AP and MP are presented in Tables 6.4 and 6.5, while the graphical presentation of the slight changes in AP and MP are presented in Figures 6.9 through 6.12. Average penetration and maximum penetration of PF (Figures 6.9 and 6.10) showed similar behavior to the effective penetration. AP and MP for PF were not affected by different level of moisture content.

Average and maximum penetration of pMDI (Figures 6.11 and 6.12) also showed similar behavior. No significant differences were found due to changes in moisture content levels.

Table 6.3. Analysis of variance of the average and maximum penetration of *Dendrocalamus strictus* culms using PF and pMDI at different levels of moisture content.

Moisture content variation	DF	Sum of squares	Mean square	F-value
Average penetration(AP):				
PF[1]	4	16538.82	4134.70	2.60 (NS)
pMDI	4	805.46	201.37	0.10(NS)
Maximum penetration(MP):				
PF[1]	4	31386.61	7846.65	2.30 (NS)
pMDI	4	18239.59	4559.90	0.97(NS)

(HS) indicates significance at the 1% level of probability
(NS) indicates not significant
1-PF type is GP806D39 for PSL

Table 6.4. Mean average penetration of adhesive (μm) of *Dendrocalamus strictus* culms using PF and pMDI at different moisture content levels.

PF[1] at different MC level				
4.0%	6.5%	7.5%	9.5%	12.0%
62.12 (24.77)	70.68 (27.43)	82.27 (17.60)	93.26 (25.42)	81.80 (25.37)
pMDI at different MC level				
4.0%	6.5%	7.5%	9.5%	12.0%
104.56 (36.27)	108.11 (45.83)	111.37 (50.26)	113.00 (48.80)	110.06 (41.30)

Table 6.5. Mean maximum penetration of adhesive (μm) of *Dendrocalamus strictus* culms using PF and pMDI at different moisture content levels.

PF[1] at different MC level				
4.0%	6.5%	7.5%	9.5%	12.0%
80.41 (38.97)	90.44 (38.83)	107.24 (28.18)	122.51 (39.05)	108.06 (38.44)
pMDI at different MC level				
4.0%	6.5%	7.5%	9.5%	12.0%
125.55 (40.64)	155.64 (90.01)	165.29 (80.68)	137.49 (57.09)	148.36 (62.34)

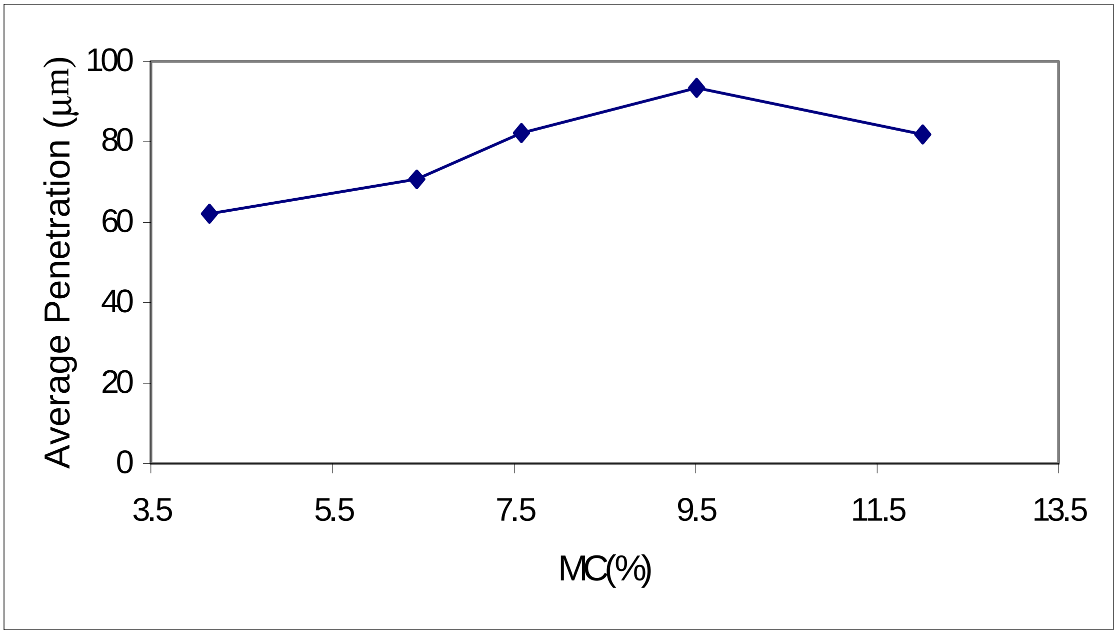


Figure 6.9. Average penetration of PF adhesive versus MC of *Dendrocalamus strictus.*

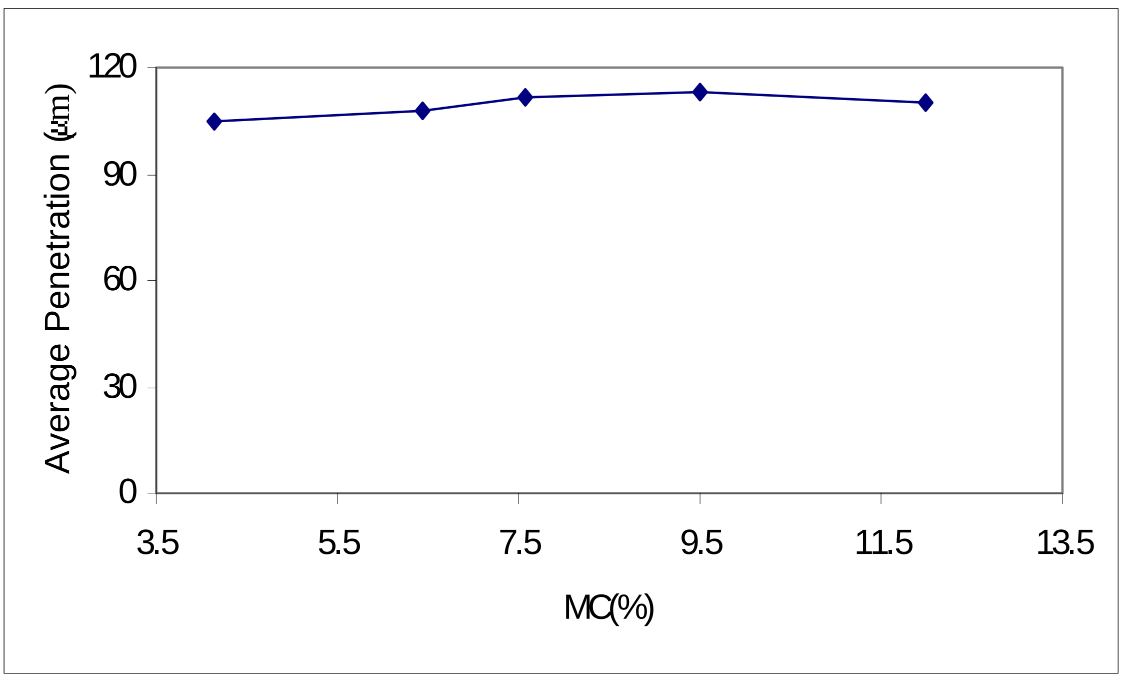


Figure 6.10. Average penetration of pMDI adhesive versus MC of *Dendrocalamaus strictus.*

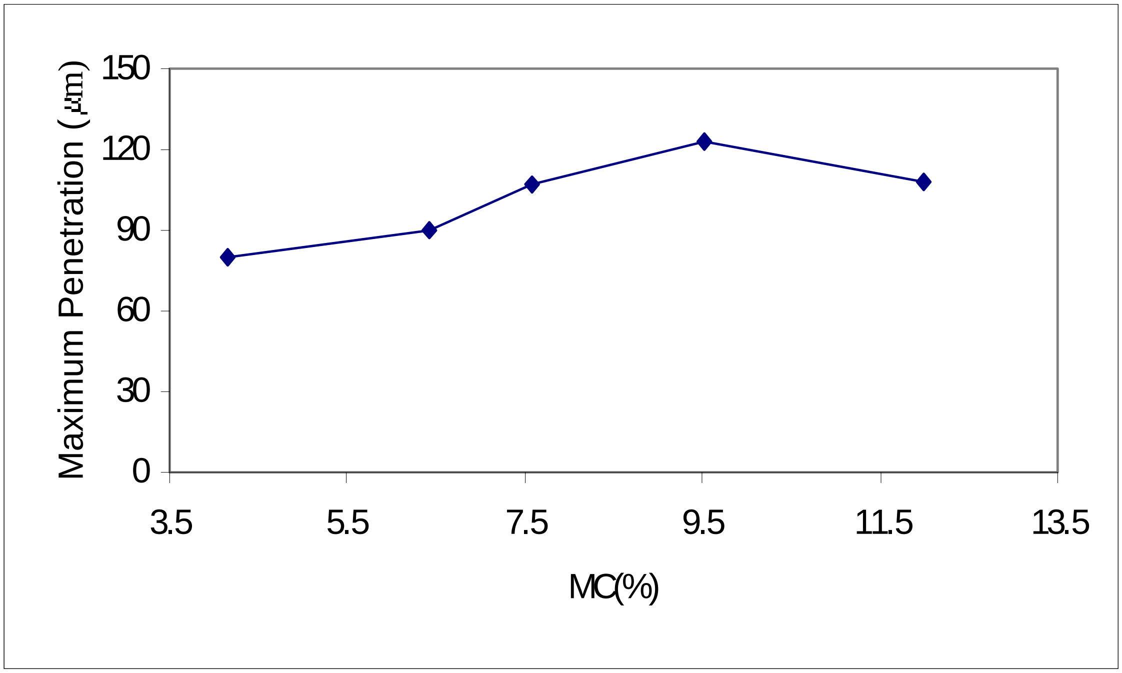


Figure 6.11. Maximum penetration of PF adhesive versus MC of *Dendrocalamus strictus.*

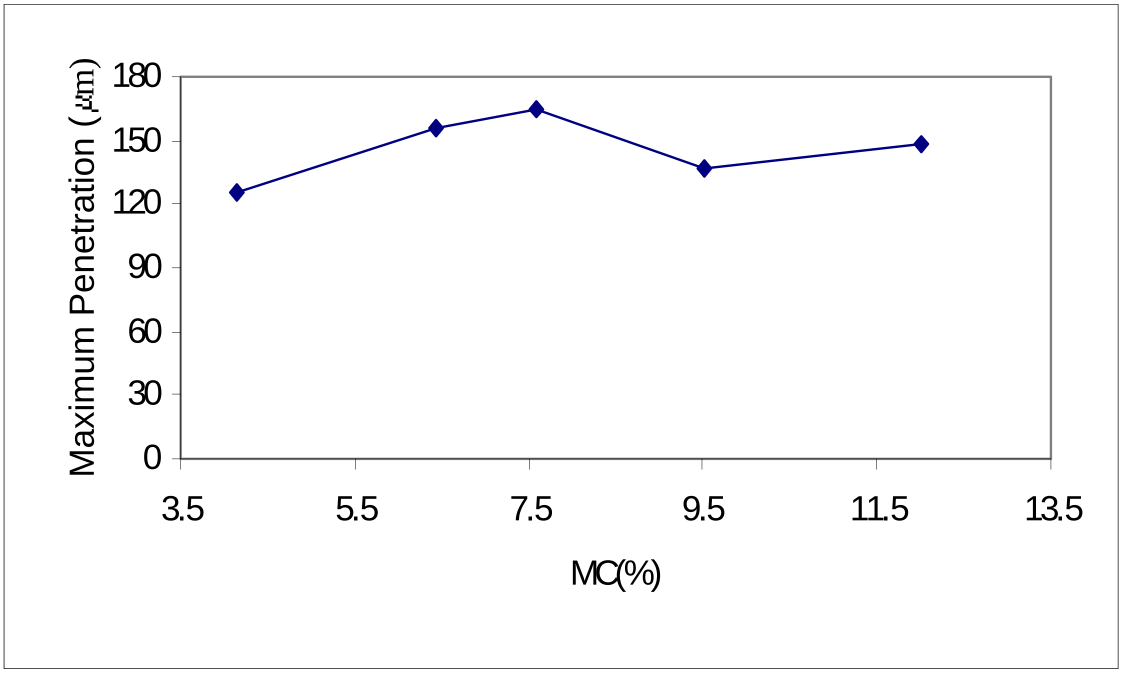


Figure 6.12. Maximum penetration of pMDI adhesive versus MC of *Dendrocalamus strictus.*

From Tables 6.4 and 6.5, the average and maximum adhesive penetration of pMDI was higher compared to the PF adhesive. The AP of PF and pMDI at 12% MC were 81.8 μm and 110.0 μm, respectively. The MP of PF and pMDI at 12% MC were 108.1 μm and 148.4 μm, respectively.

6.4 Conclusions

The adhesive penetration on Calcutta bamboo has been analyzed using two representative formulations of PF and pMDI adhesives. Effective penetration, average penetration and maximum penetration at different levels of moisture content were not significantly different from one another. There were significant differences in effective penetration between nodes and internodes, but not between the radial and tangential directions. The variability between nodes and internodes is not desirable, however the similarity between radial and tangential is a desirable behavior.

The effective penetration of the two PF resins was greater than the pMDI adhesive. On the other hand, the average and maximum penetration was greater for pMDI compares to PF.

There should not be any problem in using the three adhesives used in this study to manufacture composite from Calcutta bamboo. The adhesives flow and penetrate well on Calcutta bamboo surface. The adhesives cover the surfaces into the coarse structure, where machine damage might occur. This indicates that a good wetting condition was achieved, and a superior bond could be achieved when gluing Calcutta bamboo.

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