Chapter 5
pH and Wettability of Calcutta Bamboo

5.1 Introduction

The gluability of Calcutta bamboo is influenced by its acidity and wettability. The acidity of a material may be assessed by pH and buffer capacity. The pH value of wood or woody materials is an important criterion of its suitability for various applications [1]. The ability of the adhesive to cure on a substrate depends greatly on the condition of the surface. Since the rate of cross-linking of most thermosetting adhesives is pH-dependent, these adhesives will be sensitive to the pH of the substrate [2]. In order for the resin binders to cure properly in the board furnish, the appropriate acidity must be established [3]. The cure of urea-formaldehyde resins is accelerated in an acidic environment. However, most phenolic resins used for wood-based composite require a base environment for cure. The formulation of most adhesives is adapted to the acid range of the substrate, and a wide deviation of this value will create difficulties in providing a superior adhesive bond. Thus, pH value of any material intended for the manufacture of an adhesively-bonded composite has to be known.

Resistance of wood or woody material to the change in its pH level is called the buffer capacity. According to Maloney [3], a larger quantity of acid catalyst is required to decrease the pH to the level for an ideal resin cure when the material possesses a high buffering capacity. A single species of wood, or any woody material, that possesses high variability of buffering level could be an important issue, but becomes a critical factor when multiple species are used. In the case of Calcutta bamboo, the buffer capacity is determined in order to assist in analyzing the suitability of bamboo for use with common adhesives found in structural wood-based composite products.

One method that has been used to determine adhesive-substrate interaction is wettability [4,5]. However, wettability is not the only factor responsible for the formation of an adhesive bond. Marra [6], stated that the five steps of adhesive bonding formation in a wood substance are flow, transfer, penetration, wetting, and solidification. Wettability is one of the indicators of how well the substrate reacts with liquid. Wettability is a quick method for predicting the gluability of an unknown species [4,7]. Wetting of the surface by an adhesive is a necessary prerequisite to bond formation [7]. A convenient method to measure wetting of a solid surface is through the determination of contact angle of a liquid. Figure 1B, in Appendix B, illustrates the contact angle of a liquid on a solid surface. According to Collett [8], contact angle is an indicator of the affinity of a liquid for a solid. The shape of the liquid drop on a solid surface is related to the magnitude of the cohesion forces acting between the three planes: solid, liquid, and gas [4]. Bodig [4] and Freeman [9] used the incline wood plate, while Wellons [5] and Kalnins et al [10] used the sessile liquid drop method to determined the contact angle or the wettability. In this dissertation, the sessile drop method was used to determine the wettability and surface tension of Calcutta bamboo. This method is simple and accurate. The wetting values of the surface were reported either as contact angle or by the cosine of the contact angle. Surface tension, and other components of the surface energy, were determined using three probe liquids, namely α-bromonaphthalene (ABN), water and ethylene glycol (EG). In addition, formamide (Fo) and glycerol (Gl) were used to compare the results.

Freeman [9] studied the physical and chemical relationships between wood and adhesives. He found that the shear strength of a bond decreased with the increasing pH using urea formaldehyde, but found no apparent effect when resorsinol-phenol formaldehyde was used. Another behavior found by the researcher was that the glue-line failure increased when the pH value was high. Freeman [9] explained that, with relatively fresh and unaged joints, the pH of the wood influences the amount and quality of the polymerization and bonding to the wood surface. In another study [15], the pH value of several agriculture materials such as hemp, wheat straw, flax and grass were determined. Performance of the materials as panel products, when bonded with UF was found to be poor. The researchers relate this poor performance to the high pH value. The pH values of these agriculture materials were more than 6 and in the case of wheat straw and hemp the values were more than 7. A larger amount of catalyst had to be added in the case of high pH, otherwise the resin cures slowly and will increase the production cost. Highly acidic material will speed the cure rate when using UF adhesive. Maloney [3] explained that the effect of acidity on cure rate or press times is due to the combination of pH, buffer capacity and the existing or potential total free volatile acid content of the material. The knowledge of chemical condition of a material is a useful guideline in attempting to use it with an adhesive. Thus, pH is closely related to glue bond quality and total manufacturing cost, and must be considered as one of the important factors in determining the suitability of the raw material.

This study has four main objectives: (1) to compare the mean pH value of location 1 to 4 and determine the mean pH value for Calcutta bamboo, (2) to determine the buffer capacity of Calcutta bamboo, (3) to determine the wettability of Calcutta bamboo and the surface tension of Calcutta bamboo, and (4) to compare the wettability at locations 1 to 4, between internodes and nodes, and between radial and tangential directions.

5.2 Experimental

5.2.1 Materials

Calcutta bamboo purchased from Bamboo Rattan Works Inc. was used for the pH and wettability analysis. This bamboo, imported from Southeast Asia, had an average culm length of 5.49 m (18 ft.). Culm diameter at the bottom was about 3.3 cm (1.3 in.), while the top culm was about 2.3 cm (0.9 in.). Average thickness of the culm wall was 0.97 cm (0.38 in.). Average oven-dry density of the bamboo culm was 643 kg/m^3, while initial moisture content was about 10 to 11%. The culms were cut into 122 cm (4 ft.) lengths, and placed in a conditioning chamber for several weeks. Moisture content was monitored until equilibrium was reached (Temperature = 20^{o}C and Relative Humidity = 65%).

5.2.2 Methods

Twenty culms were randomly selected from the thirty culms purchased for various studies in this dissertation. Specimens that were selected from the culms were obtained from four locations relative to the height in the culm. Location 1 is the lower bottom part, location 2 is the upper bottom part, location 3 is the lower top part and location 4 is the upper top part. The sampling technique for each bamboo culm is illustrated in Figure 3.1 in Chapter 3. The culm sections were split into half and specimens were randomly selected for the analysis. The specimens were kept in the conditioning chamber until they were used for testing. The average moisture content of the specimens was 9.43%.

pH Value

The procedure of pH determination was adapted from the cold extraction method for hydrogen ion concentration (pH) of paper extracts, TAPPI T 509 om-83 [11]. Each specimen was ground to pass a 425-μm (40 mesh) using a milling machine (Wiley). The specimen (1g ± 0.01g) was then transferred into a 100-ml beaker and distilled water (pH~ 6.7) was added until the specimens were wet. Distilled water was added again to bring the total volume to 70-ml. The mixture was stirred well and allowed to soak for 1 hour at room temperature. A battery powered pH meter (Fisher Scientific, Accumet 1003) was used for the measurement. The pH meter was calibrated using three standard solutions, pH 4.0, pH 7.0 and pH 10.0. The electrode of the pH meter was submerged into the unfiltered mixture. The pH value was recorded when there was no more drift in the measurement for a period of 30 seconds. Analysis of variance was performed and Tukey's Studentized Range (HSD) Test was used for the comparison procedure.

Buffer Capacity

Specimens for buffering capacity were taken from the location 1 of the culm. The procedure for buffer capacity determination was adapted from the method used by Maloney [3] and Borden Chemical Inc. [12]. Specimens (10% MC) were again prepared in the milling machine and screened through a standard filter. Thirty grams of dry fibers were soaked in 400 g of distilled water (20 ± 1^{o}C) for 30 minutes. The mixture was stirred several times during the soaking. The liquid was then separated using filter paper, and 150 g of the liquid was placed in a beaker. Temperature was maintained at 21^{o}C. The pH meter was calibrated using the same method as was used for determining the pH value, and the original pH value was recorded. Titration was done using 0.01N HCl. The pH value was recorded after each acid addition. Addition was made at an increment of 0.5 ml up to 10 ml, and then with increments of 1.0 ml thereafter. A magnetic stirrer was used to mix the titration solution. The miliequivalents (N x ml) of acid needed to change the pH to 3.5 was calculated as the buffer capacity of Calcutta bamboo.

Wettability

The procedure explained by Zhang et al [13], Good [14] and others [4-10] for contact angle and surface tension measurement was used in this study. Specimens for wettability and surface tension were taken from locations 1 and 2, while specimens for comparison along the height were taken from locationa 1 to 4. Specimens at the nodes and radial direction were also taken for the comparison study. All measurements were performed on a freshly-prepared, tangential surface. Specimens were conditioned at 20^{o}C with 65% RH prior to testing. Moisture content was approximately 9 to 10%. The fresh surface was obtained by gently abrading the specimen using 220-grid sandpaper immediately before testing. All surfaces were sanded at the same rate and tested within a 2 hour period. A five-micrometer pipet was used to manually apply the drops of liquid. Images of the drops were captured by video camera within two seconds after they were applied. Comparisons between location, section (nodes and internodes), and direction were done within 10 seconds using glycerol only. At least 30 contact angle measurements were obtained for each liquid-probe, and at least 50 measurements were obtained for locations 1 to 4 using glycerol. Calculation of the bamboo surface energy was carried out using the following equation:

$$(1 + \cos\theta)\gamma_L = 2[(\gamma_s^{LW}\gamma_L^{LW})^{1/2} + (\gamma_s^{+}\gamma_L^{-})^{1/2} + (\gamma_s^{-}\gamma_L^{+})^{1/2}] \quad (5.1)$$

where γ_s^{LW} (Lifshitz van der Waals or apolar), γ_s^{+} (acid or electron accepting), and γ_s^{-} (base or electron donatiing) are the solid surface energy components, θ is the contact angle obtained by the sessile drop method for each liquid, γ_L is the liquid surface tension, and γ_L^{LW}, γ_L^{+} and γ_L^{-} are the liquid surface energy components. The liquid surface energy component for the probe liquids are given in Table 5.1.

Table 5.1. Surface tension parameters of probe liquids (mJ/m^2) [14]

Probe Liquid	γ_L	γ_L^{LW}	γ_L^+	γ_L^-
α-Bromonaphthalene	44.4	43.5	≅0	≅0
Water	72.8	21.8	25.5	25.5
Ethylene glycol	48.0	29.0	1.92	47.0
Formamide	58.0	39.0	2.28	39.6
Glycerol	64.0	34.0	3.92	57.4

All three probe liquids were used to obtain the contact angle measurements. Then, using the known liquid surface tension parameters from Table 5.1, the bamboo surface energy components were calculated by solving a set of three simultaneous equations. Formamide (Fo) and glycerol (Gl) were also used to compare the results. Total surface tension of bamboo γ_s^{total} was then calculated using the following equation:

$$\gamma_s^{total} = \gamma_s^{LW} + 2[(\gamma_s^+)(\gamma_s^-)]^{1/2} \quad (5.2)$$

Analysis of variance was performed and Tukey's Studentized Range (HSD) Test was used for the comparison between locations 1 to 4.

Statistical Test

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

$$y_{ij} = \mu + \alpha_i + \varepsilon_{ij} \qquad (5.3)$$

where:
- y = observation (properties)
- μ = mean
- α = treatment (effect of different location)
- ε = error

One-way analysis of variance with post-hoc tests was performed on the pH value and wettability. The null hypothesis for the one-way ANOVA is shown below

H_o: $\alpha_1 = \alpha_2 = \alpha_3 = \alpha_4 = 0$

H_a: At least one of the α differ from 0

The null hypothesis was that different locations (locations 1 to 4) have the same mean pH value or wettability. If the H_o is true then further tests need not to be conducted. If H_o is not true then the corresponding alternative hypothesis is H_a, at least one of the means differs from the others. In this case, the multiple comparison procedure, Tukey's studentized range (HSD) test was performed on the four culm locations.

5.3 Results and Discussion

5.3.1 pH Value and Buffer Capacity

Table 5.2 shows the analysis of variance results for pH for different locations in the culm. Analysis shows that there were no significant differences in pH value between locations. The mean pH values of locations 1 to 4 were 5.13, 5.13, 5.17 and 5.44 respectively. The overall means pH value was 5.21. Figure 5.2 illustrates graphically the comparison among the locations. Table 5B of Appendix B shows the pH values of several timber species. The pH value of Calcutta bamboo is not much different from timber species that are commonly used as structural composite product such as aspen, yellow-poplar, eastern white pine and eastern hemlock.

Table 5.2. Analysis of variance of pH value at different location along the length of *Dendrocalamus strictus* culms.

Source of variation	DF	Sum of Squares	F-value
pH	3	0.7257	4.26 (NS)

(HS) indicates significance at the 1% level of probability
(NS) indicates not significant

Table 5.3: Mean pH of *Dendrocalamus strictus*.

pH of Different Portion of Culm			
Location 1	Location 2	Location 3	Location 4
5.13 (0.23)	5.13 (0.13)	5.17 (0.26)	5.44 (0.29)
Mean pH			
5.21 (0.26)			

Number in parenthesis is associate to Standard Deviation.

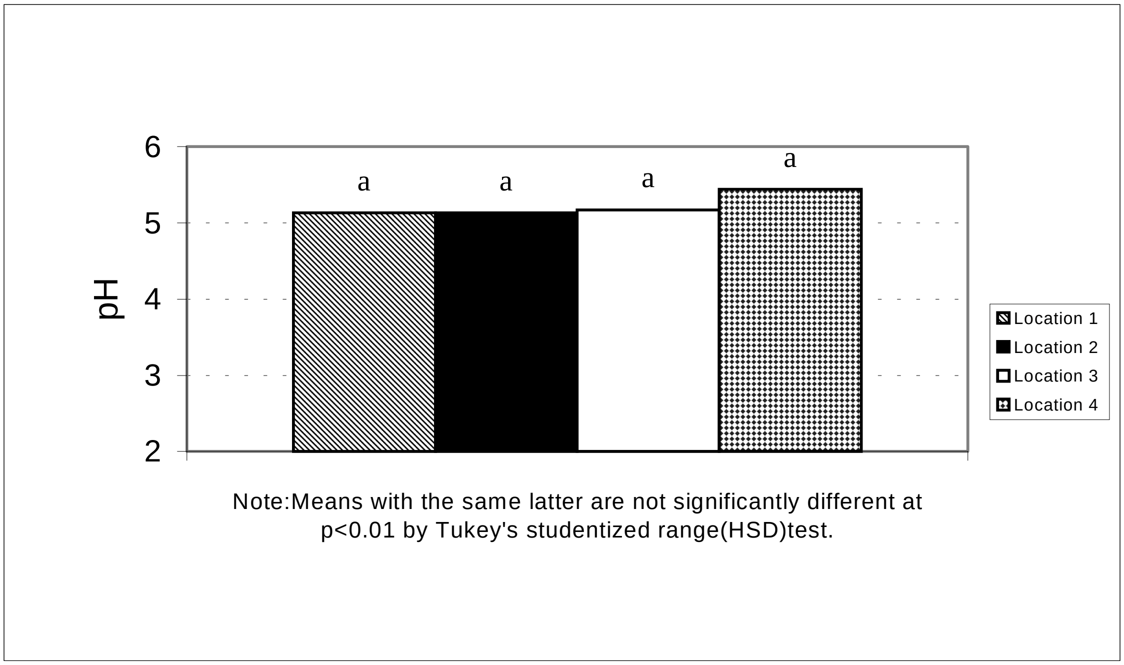

Figure 5.1. pH value of *Dendrocalamus strictus* at different locations.

Buffer capacity of Calcutta bamboo is illustrated in Figure 5.3. Initially the change was rapid for the acid addition until 10 ml was reached. The pH nearly becomes constant at a pH value of 2 after 30 ml of acid was added. Based on the acid titration, it takes approximately 6ml of acid to change the pH of the liquid to 3.5. Thus, the milliequivalents (me.), or the buffer range, of Calcutta bamboo was 0.06 (0.01N x 6ml). Table 5B in Appendix B presents the buffer range of several wood species given by Borden Chemical Inc. [12]. The buffer range of aspen and hemlock were 0.23-0.31, and 0.17-0.23 respectively, while Douglas-fir and white oak were 0.03-0.09 and 0.1 respectively.

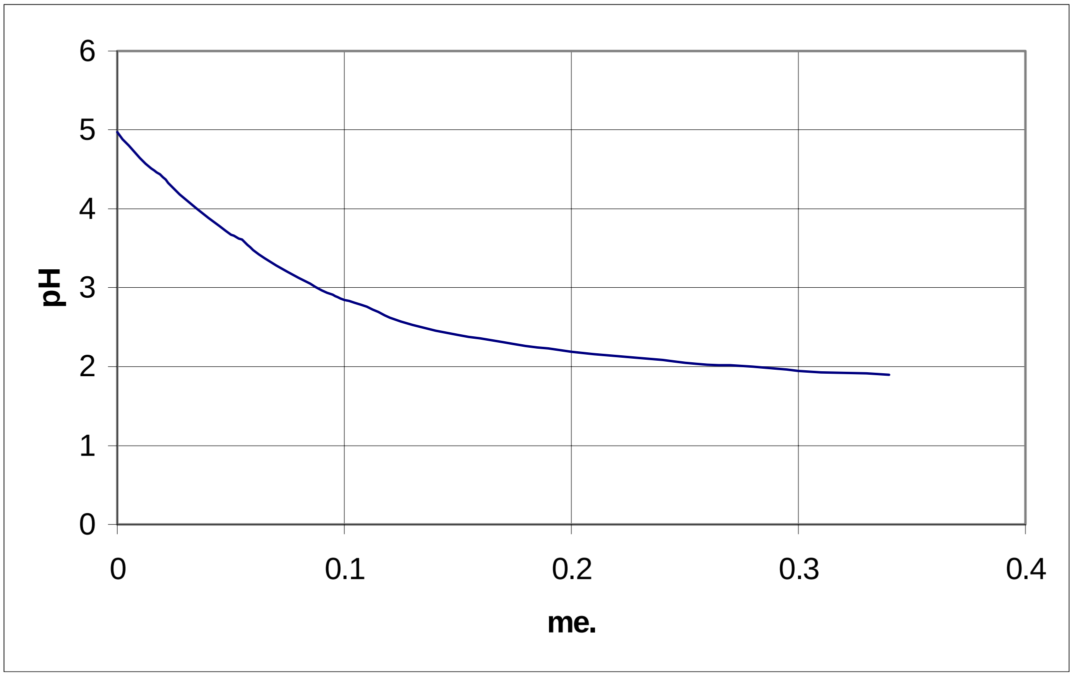

Figure 5.2. Buffer capacity of *Dendrocalamus strictus.*

Borden categorized aspen and hemlock as possessing high buffer capacity, while Douglas-fir and white oak as low buffer capacity. By this comparison Calcutta bamboo would be considered to have a low buffer capacity. Thus, it is concluded that Calcutta bamboo requires addition of a smaller amount of acid catalyst to reduce the pH to the level required for optimum resin cure. Since Calcutta bamboo has a pH value which is quite similar to many commercial timbers that are used for composite products, the same procedures and practices may be applied to Calcutta bamboo when manufacturing composites.

5.3.2 Wettability and Surface Tension

Wettability of Calcutta bamboo is reported in Table 5.4 as the mean contact angle using the probe liquids included in this study. Freeman [7] reported the contact angle of water on several timber species using the incline plate method. Although the method used in this study is different, the contact angle obtained should be approximately the same, and the values are used for comparison. Among the timber species included were aspen (*Populus tremuioides*), yellow-poplar (*Liriodendron tulipifera*) and white oak (*Quercus alba*). Contact angles of water on these timber species were 38^o, 51^o and 50^o respectively. The contact angle using water on Calcutta bamboo was 52^o. The wettability of Calcutta bamboo was very close to yellow-poplar and white oak. The smaller the contact angle, the better is the wettability. In this case, the wettability of Calcutta bamboo was less than aspen, but very close to yellow-poplar and white oak.

Average surface tension of Calcutta bamboo is reported in Table 5.5 along with values reported in the literature for several timber species. Total surface tension of Calcutta bamboo was slightly higher than yellow-poplar. From Table 5.5, the total surface tension of Calcutta bamboo was 54.3 mJ/m^2**,** while yellow-poplar was 54.0 mJ/m^2. When formamide and glyserol were used as the liquid probe, total surface energy was 62.1 and 55.4 mJ/m^2. The value comes very close to ethylene glycol. The average of total surface tension, as determined by the three liquid probes (EG, Fo and Gl), was 57.3 mJ/m^2.

Table 5.4. Mean wettability of five liquid probes.

Probe Liquid	Contact Angle (θ)	Cosine Contact Angle
Water	52.2	0.61
α-Bromonaphthalene (ABN)	13.4	0.97
Ethylene glycol (EG)	25.5	0.90
Formamide (Fo)	20.3	0.94
Glycerol (Gl)	97.4	-0.13

The surface tension characterictics of Calcutta bamboo were similar to timber since it was also dominated by the Lifshitz van der Waals component. The value of the Lifshitz van der Waals component of the surface tension for Calcutta bamboo and yellow-poplar were 44.1 and 44.6 mJ/m^2 respectively. Calcutta bamboo had a lower acid-base character than yellow-poplar, ash, maple, red oak and walnut, but was slightly greater than cherry and white oak. The acid-base character of Calcutta bamboo was dominated by the electron donating sites on its surface. This is similar to timber, which were also dominated by the electron donating sites. From the surface tension values determined in this study, Calcutta bamboo should have similar interactions with the common adhesives used with the timber species mentioned.

Table 5.5. Surface tension parameters of Calcutta bamboo and several timber species (mJ/m^2).

Material	γ_s^{LW}	γ_s^{+}	γ_s^{-}	γ_s^{total}
Calcutta bamboo:				
EG	44.1	0.89	29.2	54.3
Fo	44.1	3.00	27.1	62.1
Gl	44.1	0.00	30.2	55.4
Yellow-poplar* (*Liriodendron tulipifera*)	44.6	0.70	31.6	54.0
Ash† (*Fraxinus americana L.*)	42.6	0.001	67.4	43.2
Cherry† (*Prunus serotina* Ehrh.)	47.5	0.42	28.0	54.3
Hard maple† (*Acer saccharum Marsh.*)	45.5	0.46	33.2	53.3
Red Oak† (*Quercus rubra L.*)	39.7	0.46	37.7	48.0
White Oak† (*Quercus spp.*)	34.0	0.39	22.8	40.0
Walnut† (*Juglans nigra L.)*	37.9	0.09	58.9	42.6

* Timber species tested at the same venue and time with Calcutta bamboo
† Surface tension parameters from Gardner [16]

Comparison of the contact angle was also made between the location, section and direction in the culm. Table 5.6 presents the analysis of variance performed on the different location, section and direction. The analysis indicated that there were significant differences between the locations and sections, while there was no significant difference between the directions. Table 5.7 shows the mean contact angle for the source of comparison made in this study. The mean contact angles of locations 1 to 4 were 55.8^{o}, 56.6^{o}, 54.6^{o} and 52.4^{o}, respectively. From Figure 5.3, the Tukey's studentized range (HSD) test performed at 99% confidence level, showed that the only significant difference occurred between locations 2 and 4.

The contact angle of the nodes was significantly greater than the internodes under the same statistical test procedure. The contact angles for nodes and internodes were 77.4^{o} and 57.6^{o}. An explanation for this behavior may be a higher extractive content at the nodes compared to the internodes. The extractive, or chemical, composition of Calcutta bamboo was not investigated here, and no previous studies could be found. However, the darker color of the nodes could be caused by a higher extractives content or a change in constituents proportions.

Table 5.6. Analysis of variance of contact angle for glyserol at different location, section and direction of *Dendrocalamus strictus* culms.

Source of variation	DF	Sum of Squares	Mean Square	F-value
Location	3	571.04	190.35	3.96 (HS)
Section	1	5844.90	5844.90	48.99 (HS)
Direction	1	0.79	0.79	0.02 (NS)

(HS) indicates significance at the 1% level of probability
(NS) indicates not significant

Table 5.7. Mean contact angle using glycerol at different location, section and direction of *Dendrocalamus strictus* culm

Different Internodes Location			
Location 1	Location 2	Location 3	Location 4
55.8 (8.79)	56.6 (6.18)	54.6 (5.94)	52.4 (6.63)
Nodes and Internodes			
Nodes		Internodes	
77.4 (14.64)		57.6 (7.48)	
Radial and Tangential			
Radial		Tangential	
57.8 (6.43)		57.6 (7.48)	

Number in parenthesis associate to Standard Deviation.
All units in degree

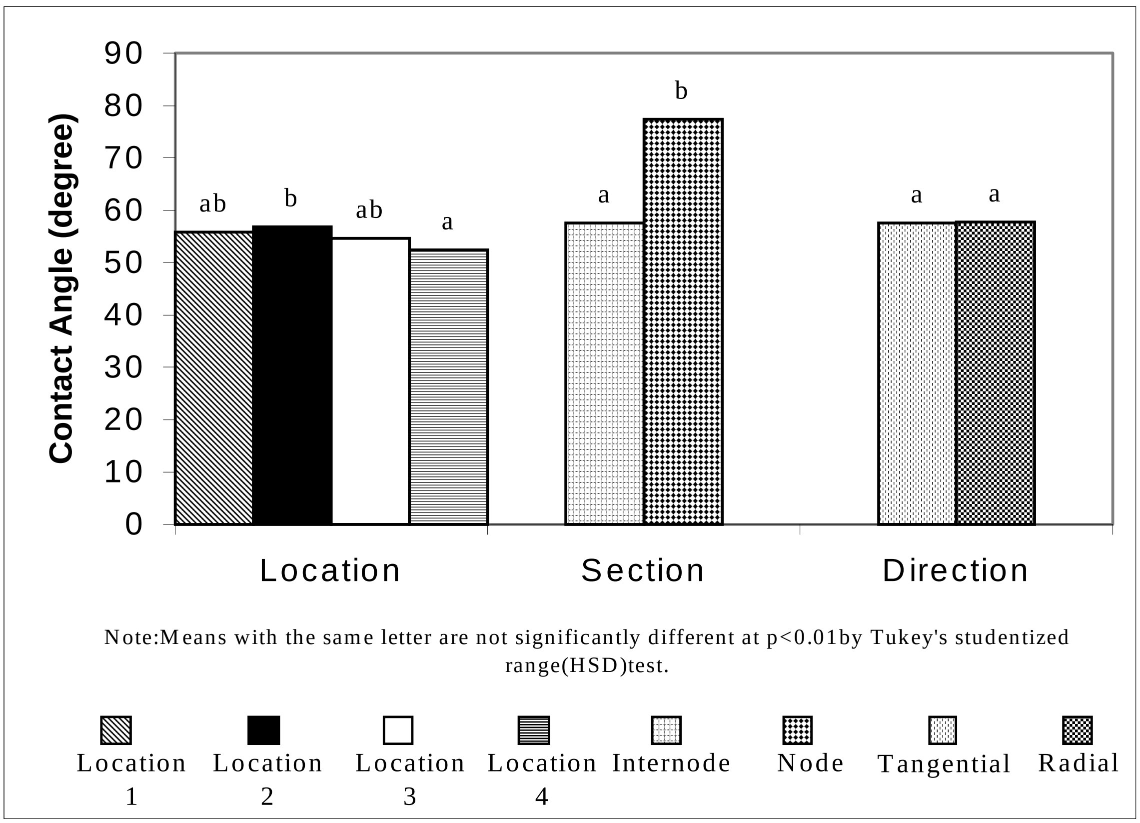

Figure 5.3. Mean contact angle of *Dendrocalamus strictus* at different location, section and direction using glycerol.

Another explanation for this behavior may be the different anatomical structure of the nodes. Grosser et al [22] explained that the nodes have an irregular interwoven texture formed by the vascular bundles, and that fiber strands and lateral sclerenchyma shealths of the metaxylem vessels are absent.

The contact angle of the radial and tangential directions were not significantly different from each other. As shown in Table 5.7, mean contact angle for glycerol on Calcutta bamboo in the radial and tangential directions was 57.8 and 57.6 degrees, respectively.

5.4 Conclusions

Generally, Calcutta bamboo has comparable pH, buffer capacity, and wettability to timber species commonly utilized in composite products. The wettability of the radial and tangential directions were similar to each other. The pH value and wettability were shown not to be affected by location along the culm. From a practical point of view, this is a desirable behavior because a variation in pH value at different culm locations could complicate the gluing process. Buffering capacity of Calcutta bamboo was shown to be similar to wood. Wettability and the surface tension were found to be similar to many commercial timber species that are used in composite products. However, wettability of nodes was found to be lower than internodes, which may impose some variability in adhesive bonding.

5.4 References

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