Thermal softening of rattan canes: influence of the hemi cellulose-lignin matrix

W. P. ABASOLO [1,*], M. YOSHIDA [2], H. YAMAMOTO [2] and T. OKUYAMA [2]

[1] *Department of Forest Products and Paper Science, College of Forestry and Natural Resources, University of the Philippines Los Baños, Laguna 4031, Philippines*
[2] *Bio-material Physics Laboratory, Graduate School of Bioagricultural Sciences, Nagoya University, Chikusa, Nagoya 464-8901, Japan*

Abstract—The influence of the hemicellulose–lignin matrix of the cell wall of eight rattan species on the thermal softening of cane was evaluated using the creep compliance test. Extractive free samples were first prepared using ethanol–benzene. This was followed with the chemical analysis of the rattan cell wall using standard procedures used in wood. Results revealed that the cell wall is 42–53% alpha-cellulose, 19–27% hemicellulose and 20–40% lignin. The creep compliance test showed the softening behaviour of the samples due to the application of heat. Softening occurred from 70–85°C for extractive-free, 75–95°C for holocellulose and 100°C for alpha-cellulose samples. For the eight species, variation in the degree of thermal softening was observed. This was attributed to the differences in the proportion of hemicellulose–lignin matrix between species: the higher the volume of the matrix, the larger was the observed molecular movement. Reduction in thermal softening values from the extractive-free materials to the holocellulose and up to the alpha cellulose samples was also noticed. This is parallel to the reduction in the matrix volume because of the removal of lignin. Alpha-cellulose still exhibited some movement. Such movement can only be derived from the crystalline–amorphous region within the cellulose chain. The more crystalline the material, the smaller was the observed molecular movement.

Key words: Thermal softening; creep compliance; extractive-free sample; holocellulose; alpha-cellulose; lignin; hemicellulose; maximums softening.

INTRODUCTION

Rattan canes are long slender materials commonly found in tropical countries. One unique characteristic of this material is its flexibility. With the application of a suitable amount of heat, the cane can be moulded, curved, changed in shape indefinitely without significantly altering its mechanical properties. Because of

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*To whom correspondence should addressed. E-mail: willieabasolo@yahoo.com

Table 1.
Species used in the analysis

Common name	Scientific name	Diameter (cm)
Palasan	*Calamus merrillii* Becc.	3.0–3.5
Lasun	*Calamus ornatus* Bl.	2.5–3.0
Semambu	*Calamus scipionum* Lour.	2.5–3.0
Batang	*Daemonorps robustus* Warb.	2.5–2.7
Batu	*Calamus subinermis* H. Wendi	2.5–2.7
Bakau	*Calamus erinaceus* (Becc.) J. Dransf.	2.5–2.7
Tunduan	*Calamus ornatus* Bl.	3.0–3.5
Manau	*Calamus manau* Miq.	2.8–3.0

this, it is extensively used in the furniture industry. In order to further exploit this property of the cane, one needs to analyse its softening behaviour.

Thermal softening is an instantaneous and reversible physical process [1] involving the movement of cellulose molecules within the softened hemicellulose–lignin matrix due to the application of heat. This allows the moulding or the reconfiguration of the material to a well-determined shape. Heat affects the softening of wood in three ways: first it degrades the hemicellulose; then it increases the regularity of the crystalline lattice; finally, it decomposes the lignin–hemicellulose matrix [2]. In so doing, controlled heat treatment can also release residual growth stresses in trees reducing the occurrence of detrimental drying defects [3].

Normally, softening in wood is measured by observing the rate of movement of a wood strip under a constant load at a steadily increasing temperature [4]. However, lately, Dwianto *et al.* [2] noticed the advantage of using creep measurements in detecting structural changes in wood caused by heat. With this, Abasolo *et al.* [5] were able to detect the softening point of rattan canes using match-ending blocks. Though they noticed the influence of hemicellulose on rattan softening, the possible effect of material anisotropy along its three cardinal planes was yet to be considered. Thus, the exact role of the hemicellulose–lignin matrix on cane softening was not clarified.

The present study deals with the determination of the softening behaviour of eight rattan species (Table 1). The main goal of this study is to try to define the role of the hemicellulose–lignin matrix on the softening behaviour of the cane.

MATERIALS AND METHODS

Sample preparation

Eight rattan species were used in the analysis (Table 1). The individual samples were reduced to powder with a Wiley mill. To reduce the possible influence of varying powder sizes on molecular movement caused by heat, only samples

that pass through an 80-mesh wire screen were gathered. From these powders, extractive-free samples were prepared using ethanol–benzene (1 : 2) for 8 h.

Chemical analysis

Following the 1975 ASTM standards, holocellulose [6], alpha-cellulose [7], and lignin contents [8] of the extractive-free samples were determined. Average of two measurements was used in the evaluation. Holocellulose and alpha-cellulose samples were then collected for creep compliance measurements.

Creep compliance

The creep compliance of the extractive-free, holocellulose and alpha-cellulose samples at constant temperature was determined with a thermo-mechanical analyser (Seiko, TMA/SS6000). This was done to evaluate the influence of heat on sample softening. The temperature settings used in the analysis were from 35°C to 100°C with a 5-degree interval.

First, 0.010–0.015 g of the sample was packed in a 5 mm diameter aluminium pan. The sample was then covered with an aluminium cover and was soaked overnight in water. The following day, it was compressed for 5 min at a constant load of 2 N/mm^2 with an Imada pull-push scale apparatus (Fig. 1a). This was performed to allow the powder to set-in uniformly in the pan. Then, they were soaked again in water prior to creep measurement. A total of 28 samples was prepared, two samples for every temperature setting.

After calibration, the sample pan with the sample powder was placed at the centre of the sample tube (Fig. 1b) and an initial compressive load of 5 g was applied. Immediately, the whole set-up was submerged in water and temperature was adjusted to the desired setting. This setting was maintained for 5 min to allow water and sample temperature to equalize. Finally, the load was raised to 150 g, probe height was reset to zero then creep measurement was performed. The amount of strain at constant temperature was measured for 10 min. Creep compliance was computed using the formula:

$$S(t) = \varepsilon(t)/\sigma_0, \tag{1}$$

where $S(t)$ is the creep compliance in MPa^{-1}, $\varepsilon(t)$ is the amount of strain at time t and σ_0 is the amount of applied stress in MPa. Average creep compliance of two measurements for every temperature setting was used in the analysis.

Statistical analysis

Analysis of variance (ANOVA) was performed to determine the variation in the proportion of the chemical constituents among species. Variation in the average thermal softening between samples (extractive-free, holocellulose and alpha-cellulose) and within the individual species was also evaluated. In analysing
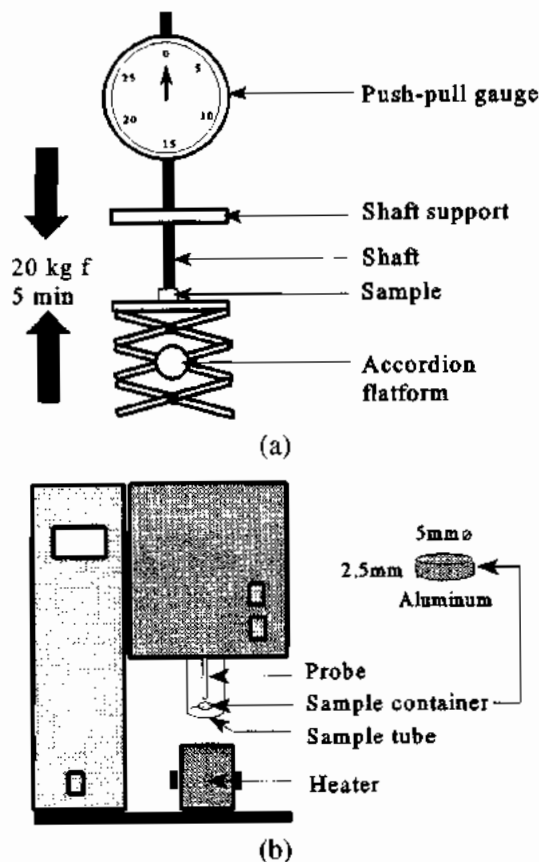
Figure 1. Apparatus used in the analysis. (a) Imada push-pull scale with a digital force gauge. (b) Thermomechanical Analyzer (TMA).

the softening behaviour of the cane, the standardized maximum softening values of the individual samples were utilized. This value was derived using the formula:

$$Z = \frac{x - \bar{x}}{s}, \tag{2}$$

where Z is the standardized value, x is the maximum thermal softening of a particular temperature (MPa^{-1}), $\bar{x}$ is the average thermal softening of that temperature setting (MPa^{-1}) and s is the standard deviation.

RESULTS AND DISCUSSION

Chemical analysis

The plant cell wall is basically composed of three major components; cellulose, hemicellulose and lignin. Cellulose is a linear homopolymer of anhydro-β-D-glucose joined together by glycosidic bonds [9]. Hemicellulose resembles cel-

Table 2.
Proportion of the major chemical constituents of the cell wall of rattan

Species	Alpha-cellulose (%)		Hemicellulose (%)		Lignin (%)
(a) Summary					
Palasan	44.8		32.2		22.2
Lasun	48.6		30.3		19.3
Semambu	42.3		30.1		24.1
Batang	38.8		31.7		37.0
Batu	40.4		31.3		27.7
Bakau	32.0		33.3		40.1
Tunduan	41.7		31.3		22.2
Manau	50.8		28.4		23.6
(b) Statistical analysis (ANOVA)					
Sources of variation	SS	df	MS	F_{com}	F_{tab}*
a. Between the three chemical constituents	1019.69	2	509.85	16.40	3.47
b. Between species	653.22	21	31.10		
Total	1672.92	23			

*$\alpha = 5\%$. Note: SS = sum of squares, df = degree of freedom, MS = mean square.

lulose being built largely of anhydro-β-D-glucose, β-D-mannose, and β-D-xylase. However, due to the formation of side groups, it has very different properties [10]. Finally, lignin is an amorphous material made up of hydroxylated and methoxylated phenylpropane units bonded together by ether and carbon–carbon bonds [11]. The individual characteristics of these three components highly influence both the plastic and elastic behaviour of wood [12].

Based on dry weight, alpha cellulose content of the canes ranged from 42–53%, hemicellulose was from 19–27%, and lignin varied from 20–40% (Table 2a). These values did not differ much from the chemical composition of bamboo [13] or from the alpha-cellulose in Douglas-Fir [14]. Statistical analysis revealed (Table 2b) a significant variation in chemical composition among the eight species. This variation could be attributed to the differences in cellular make-up of the individual samples. Tissue percentage of the cane tends to change not only across its radius but also along its length [15]. Because the proportion of the cell wall constituents of different types of cells differ from one another [16], the overall chemical composition of the individual species also showed a great deal of variation.

Considerations prior to creep measurements

The TMA apparatus has the ability to detect very small changes in sample length (up to 0.02 μm) brought about by the load and heat. These changes are derived either from the compression of the particles due to the load or by molecular movement

within the sample due to heat. Because of the smallness of such movement, two considerations were taken prior to measurements:

(i) *Influence of sample moisture content*

Water softens wood [17]. Molecular and capillary sorption of water molecules result in an increase in the distance between crystallites even at low temperatures [18]. Such an increase will weaken the dipole moment of the hydroxyl groups leading to greater molecular mobility. For this reason Zhou *et al.*, [19] observed a linear change in mechano-sorptive creep with an increase in sample moisture content.

The apparatus used in this experiment is designed for dry heating. As the sample is heated up, its moisture content (MC) will vary. This will eventually result in sample shrinkage as well as thermal expansion. Thus, the actual molecular movement of the sample will be difficult to assess. Therefore, sample MC should be maintained throughout the experiment. To achieve this, the instrument was slightly modified to allow the use of water as the heating medium. In so doing, only the influence of heat on sample softening was isolated.

(ii) *Influence of sample anisotropy*

Thermal softening of rattan depends on the species and on its inherent morphological variations [20]. Such variation could be attributed to the way the different cells that make up the stem are arranged within its structure [19]. Similar to wood, the way the different cells that comprise rattan canes could lead to the anisotropic behaviour of the cane including its thermal softening [21]. As a solution, fine sample powder (80-mesh) was used in the experiment instead of small sample blocks.

Packing the sample inside the aluminium pan could also cause sample anisotropy. Comparing a loosely packed sample to a tightly packed specimen, it is logical that molecular movement of the former will be larger than the latter. To eliminate this possibility, the amount of sample placed in the pan was more or less the same (0.010–0.015 g). In addition, the load applied for the powder to set in the pan prior to measurement was kept at 2 N/mm^2 for 5 min. With this, sample preparation was conducted in a more or less similar manner.

Creep compliance

Figure 2 shows examples of creep compliance curves of Palasan and Lasun for the three types of specimens (extractive-free, holocellulose, alpha-cellulose). The generated compliance curves were characterized by an instantaneous creep in the first 5 min followed by a gradual increase in compliance until it levelled off at a certain point. Based from the figure, variation in maximum compliance of the different temperature settings can be observed. Compliance values ranged from 5 to 16 MPa^{-1} in Palasan and from 4 to 13 MPa^{-1} in Lasun. This variation was greatly reduced in the case of both holocellulose and alpha cellulose samples. In
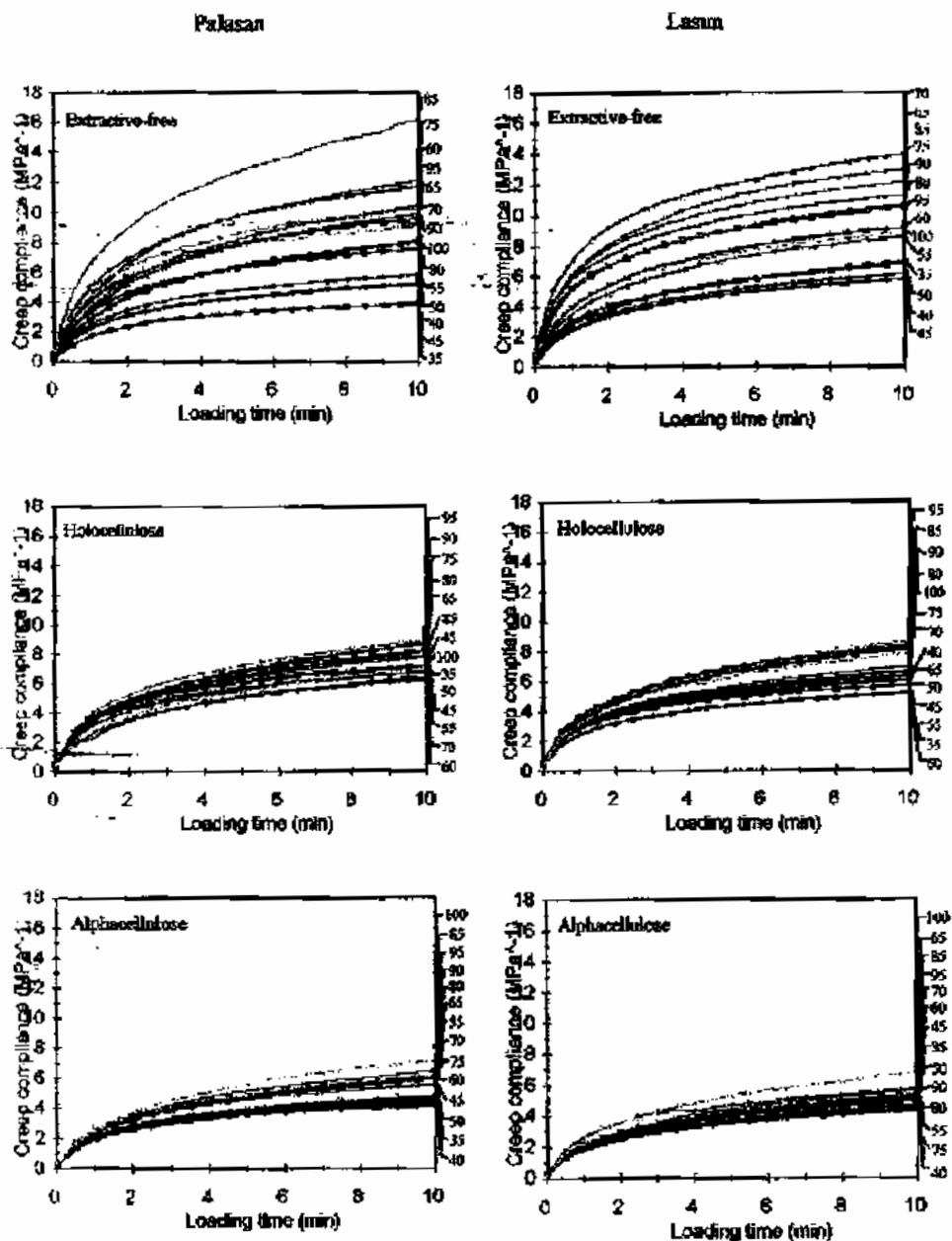
Figure 2. Examples of creep compliance curves of Palasan and Lasun canes.

both samples, the individual curves tend to aggregate with one another. Because of this clumping together of the curves, it would imply that the amount of molecular movement brought about by heat was significantly alleviated. As for the rest of the sample species, e.g. Semambu, Batu, Bakau, etc. similar behaviour was observed.

Softening behaviour of the three samples

A single compliance curve of a particular temperature is an expression of how the material behaved at that temperature. To describe the overall softening behaviour of the material as influence by heat, the average creep compliance of the individual temperature setting was taken and plotted against temperature (Fig. 3).
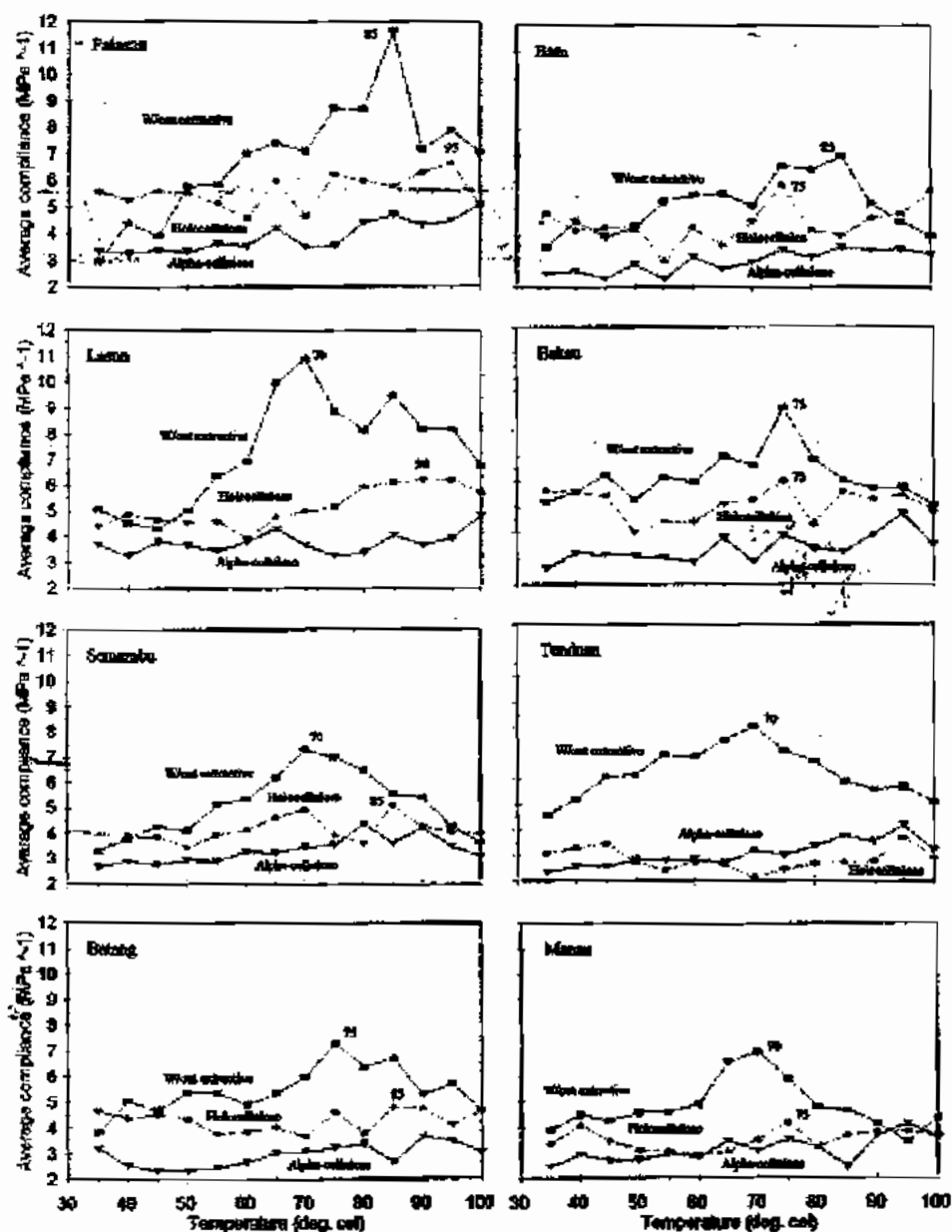

Figure 3. Softening behavior of the different samples.

In general, at the initial stages of heating (35–50°C), the curve was characteristically flat. This would imply that, at this stage, the samples were not affected yet by heat. Beyond this point (55°C), sudden changes in values were then detected. It was therefore deduced that sample softening begins at this temperature. It then steadily increased until the maximum point was achieved followed by a gradual decrease in softening.

Maximum softening of extractive-free and holocellulose samples gave a great deal of variation between species (Table 3). For example, in extractive-free Palasan samples, it occurred at 85°C while in Lasun it was at 70°C. In holocellulose samples of Semambu, maximum softening was at 85°C while in Manau, it was at 75°C. These peaks are good indicators of the molecular mobility of the materials caused by heat. The higher the softening peaks, the larger the molecular mobility of the samples. As for alpha-cellulose, distinct peaks were not observed. This only verified that fact that alpha-cellulose will only soften at 230°C [22].

Finally, the extractive-free samples were observed to give the highest softening values. This was followed by holocellulose and then by alpha-cellulose. The implication of this result would mean that the extractive-free samples were more pliable than the other two sample types. However, before making a general conclusion, one needs to consider the possible influence of the changes in matrix volume on molecular movement. It seems that, as the level of the hemicellulose–lignin ma-

Table 3.

Statistical analysis on the softening behavior of the cane

Species	Extractive-free			Holocellulose			Alpha-cellulose		
	Mean	Std. Dev.	CI($\pm$)*	Mean	Std. Dev.	CI($\pm$)*	Mean	Std. Dev.	CI($\pm$)*
(a) Summary									
Palasan	6.82	2.13	0.997	5.59	0.59	0.319	3.90	0.58	0.318
Lasun	7.33	2.02	1.099	5.15	0.72	0.389	3.76	0.41	0.222
Semambu	5.12	1.24	0.673	4.07	0.50	0.272	3.30	0.49	0.266
Batang	5.46	0.87	0.472	4.27	0.39	0.212	2.92	0.42	0.227
Batu	5.10	1.02	0.558	4.43	0.70	0.384	2.97	0.41	0.222
Bakau	6.18	0.93	0.508	5.11	0.57	0.310	3.38	0.54	0.291
Tunduan	6.24	0.96	0.522	2.82	0.40	0.220	3.05	0.49	0.264
Manau	4.96	1.05	0.573	3.48	0.39	0.212	3.12	0.49	0.265

*α at 5%.

(b) Analysis of variance

Sources of variation	SS	df	MS	F_{com}	F_{tab}*
a. Between the three types of samples	27.36	2	13.68	23.40	3.47
b. Between species	12.28	21	0.58		
Total	39.64	23			

*α = 5%.

trix was reduced, the softening values were also reduced. Such possibilities will be discussed later.

Significance of the hemicellulose – lignin matrix on the softening behaviour of the cane

Lignin is chemically linked to hemicellulose [23, 24]. Studies showed that in grasses, hemicellulose and lignin are bridged together by ester or ether linked *p*-coumaric and ferulic acids [25]. Other materials are sometimes included in the matrix, e.g. pectin and proteins [26], but because of their scarcity, the general behaviour of the matrix will largely depend on this hemicellulose – lignin link-up.

Influence of the matrix on the maximum softening of the material. In order to compare the maximum softening of the individual samples, the standardized maximum softening (Z-value) was used in the analysis. With this value, the standard deviation in sample softening of the individual temperatures with respect to the average softening of the material was considered in the evaluation (Table 4). These standardized values were then compared to the percentages of hemicellulose – lignin matrix, hemicellulose content and lignin content (Fig. 4).

Hemicellulose – lignin matrix directly affected the standardized maximum softening of the canes. As the percentage of the matrix increased, the Z-values of the samples also increased (Fig. 4a). This means that the volume of the hemicellulose – lignin matrix highly influenced the mobility of the cellulose constituents within the walls. When the hemicellulose (Fig. 4b) and lignin (Fig. 4c) component of the matrix were separately compared to the Z-value, both parameters highly influenced the standardized maximum softening of the samples. Thus, it further proved the important role of both components in the softening of the cane. Comparing their coefficient of regression (r), the contribution of hemicellulose to the molecular mobility of the samples was observed to be slightly higher than the influence of lignin. This may be because of the thermal-chemical sensitivity of the

Table 4.
Standardize maximum softening of the rattan species

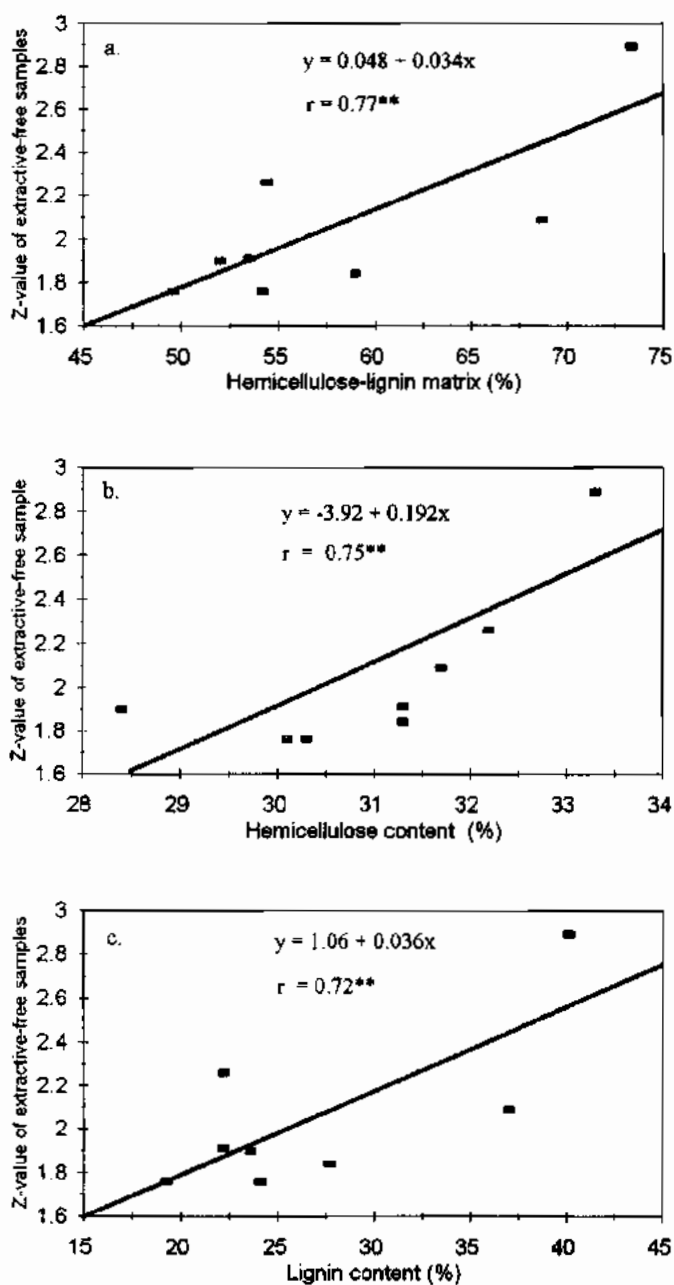| Species	Extractive-free		Holocellulose		Alpha-cellulose	
	Peak	Standardize (Z)	Peak	Standardize (Z)	Peak	Standardize (Z)
Palsan	11.64	2.26	6.64	1.78	5.09	2.05
Lasun	10.89	1.76	6.21	1.47	4.81	2.56
Semambu	7.30	1.76	5.09	2.04	4.36	2.16
Batang	7.28	2.09	4.78	1.31	3.64	1.17
Batu	6.98	1.84	5.88	2.07	3.53	1.36
Bakau	8.87	2.89	6.02	1.60	4.74	2.52
Tunduan	8.07	1.91	3.67	2.12	4.16	1.88
Manau	6.69	1.90	4.19	1.82	4.15	1.88

Figure 4. Influence of the percentage hemicellulose–lignin matrix (a), hemicellulose (b), and lignin (c) on the softening behavior of the extractive-free samples.
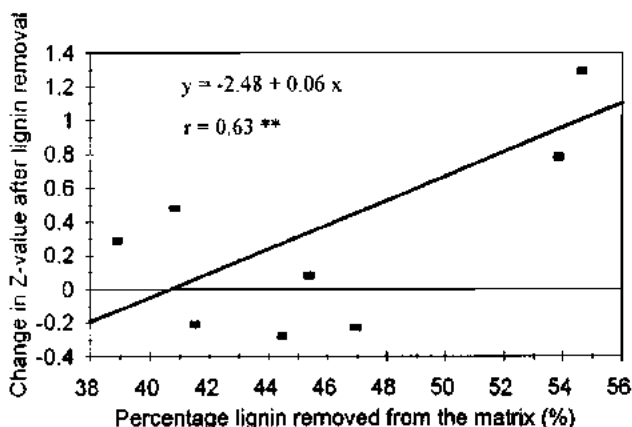
Figure 5. Effect of lignin removal from the matrix on the reduction of softening values from the extractive-free samples to the holocellulose samples.

hemicellulose component similar to the observation of Winandy (1995) as cited by Sweet and Winandy [27] in fire-retardant treated pine.

Influence of the matrix on the reduction in the maximum softening of the samples. As pointed out earlier, there was a tendency for the softening of the materials to decrease after the removal of lignin. For example, considering the mean softening of Palasan canes (Table 3), from a value of 6.82, it was reduced to 5.59 after lignin was removed. To explain this, the standardized maximum softening (Z-value) of the individual samples was again used in the analysis. This was done by taking the difference in Z-value of the extractive-free samples and the holocellulose samples (extractive-free$_{Z\text{-value}}$ $-$ holocellulose$_{Z\text{-value}}$) and comparing it with the percentage of lignin removed from the matrix [(matrix $-$ lignin/matrix) $\times$ 100]. Regression indicated that these two variables were directly related with each other (Fig. 5). As the amount of lignin removed from the walls increased, reduction in the standardized maximum softening of the samples also increased. Thus, the decrease in softening values from the extractive-free to the holocellulose samples was not mainly because the former was more pliable than the latter but was also due to the removal of lignin, which resulted in the reduction in the volume of the wall matrix. This is logical because the degree of mobility of the cellulose component will definitely be affected by the volume of the matrix: the larger the matrix volume, the larger the space available for the cellulose to move into. Similarly, the decrease in wall matrix volume could explain the decline in softening values from holocellulose to alpha-cellulose.

Softening of holocellulose and alpha-cellulose

To further prove the significant influence of hemicellulose on the softening of the sample, the Z-value of the holocellulose samples was compared to the percentage
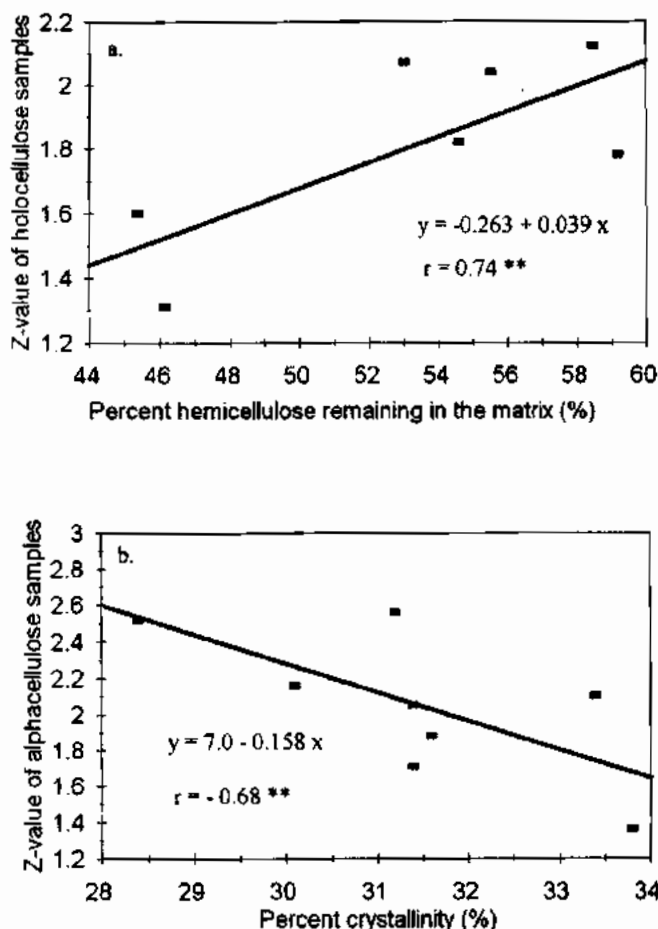
Figure 6. Softening behavior of holocellulose and alphacellulose. Influence of hemicellulose content on the maximum softening of holocellulose (a), and influence of alpha-cellulose crystallinity on the maximum softening of alpha-cellulose.

hemicellulose remaining in the matrix after lignin was removed (Fig. 6a). Regression showed that the two were highly correlated with each other. As the proportion of hemicellulose remaining in the matrix increases, maximum softening of the material also increases. This shows how the hemicellulose component of the walls promoted material softening. The higher the hemicellulose content, the higher the molecular mobility caused by heat.

Isolated cellulose still showed some movement. This movement could only be attributed to the basic composition of the cellulose chain. Generally, cellulose is made up of two distinct regions; the crystalline region and the amorphous region [28]. To check the influence of these regions on molecular movement, percent crystallinity of the alpha cellulose samples was measured using a X-ray diffractometer (Shimadzu, XD-w1) and the results were compared to its corresponding Z-value (Fig. 6b). Re-

gression showed that as percent crystallinity of alpha-cellulose increases, maximum softening of the sample decreases. Therefore, the more crystalline the material, the more it inhibited molecular movement caused by heat.

CONCLUSION

The cell wall of rattan possessed more or less the same amount of alpha-cellulose (42–53%), hemicellulose (19–27%) and lignin (20–40%) as wood. Using the creep compliance test, softening caused by heat was detected in all the samples. Softening began at 55°C regardless of the type of samples used. As the hemicellulose–lignin matrix softens, cellulose is able to move freely within the cell wall until the matrix starts to harden again. The degree of thermal softening varied between species. This was attributed to their differences in the proportion of hemicellulose–lignin matrix: the higher the volume of the matrix, the larger was the observed molecular movement. Thermal softening values were highest in the extractive-free samples followed by the holocellulose samples and finally, by the alpha-cellulose samples. This reduction was associated with the reduction in the matrix volume caused by the removal of lignin. Alpha-cellulose still exhibited some movement. Such movement can only be derived from the ratio of the crystalline to the amorphous phase within the cellulose chain: the more crystalline the material, the smaller was the observed molecular movement.

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