Rattan Cane Modified with Polyethylene Glycol Melamine-Urea-Formaldehyde Resin

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To effectively improve the strength of *Plectocomia pierreana* rattan cane without reducing its toughness, the cane was impregnated with a new water-soluble melamine-urea-formaldehyde (MUF) resin modified with low-molecular-weight polyethylene glycol (PEG), marked as PMUF. The PMUF synthetic process was optimized using an orthogonal test $L_9(3^4)$. Results showed that the dimensional stability, density, and most mechanical properties of modified canes were improved greatly. Compared with MUF, PMUF imparted the cane with higher anti-swelling efficiency (ASE), modulus of elasticity (MOE), modulus of rupture (MOR), and impact toughness. These improvements indicated that PMUF could effectively improve the cane's dimensional stability and strength, while simultaneously retaining its flexibility. Based on a comprehensive evaluation, the optimum modification conditions were: PEG-400, PEG/Melamine mole ratio of 0.1, step-wise synthesis, and PMUF solution of 30%. The ASE of optimal modified canes reached 65.51%, and its mechanical properties such as the MOE, MOR, compressive modulus, and compressive strength increased by 135.61%, 129.01%, 106.22%, and 88.52%, respectively. Additionally, its impact toughness was only reduced by 6.85%. The PMUF modified *P. pierreana* canes is comparable to the commercial *Daemonorops margaritae* canes.

Keywords: Rattan cane; PMUF resin; Impregnation treatment

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INTRODUCTION

Rattans have been described as the world's most important non-timber forest product, due to their flexibility and high strength (Lv *et al.* 2012; Charles *et al.* 2013). Rattan cane is a good furniture making material (Ariffin *et al.* 1992; Hisham *et al.* 2014); however, it is easily fractured in practical application (Lv *et al.* 2012). In China, about 42 species and 26 varieties of rattans can be found, but only 4 species are exploited, including *Daemonorops margaritae, Calamus tetradactylus, Calamus simplicifolius,* and *Calamus egregius,* while the others are barely used. *Plectocomia pierreana* grows rapidly and abundantly in the tropical area of China, but the cane cannot be used owing to its inferior physical and mechanical properties (Bhat and Thulasidas 1991; Ariffin *et al.* 1992; Wu and Chen 2003; Norul 2011). Thus, it is urgent and important to explore a technique to improve cane properties, which could not only prolong the service life of cane products, but also promote the development of inferior rattan canes (Norul 2011; Hisham *et al.* 2014).

Ariffin *et al.* (1992) made an attempt to modify rattan canes with phenol formaldehyde resin, leading to a great increase in the modulus of rupture (MOR), compression, and shear strength. So far, many researchers have confirmed that water-soluble resin impregnation treatments can impart advantageous properties in both rattan and wood, including increased moisture resistance, decreased swelling, shrinkage, increased modulus of elasticity (MOE), modulus of rupture (MOR), resistance to biological deterioration, and fixation of compressive deformation (Deka and Saikia 2000; Gindla and Gupta 2002; Gindla *et al*. 2003; Huang *et al.* 2013; Huang *et al.* 2014). However, resin modification can also cause a significant reduction in material’s flexibility and make it brittle, especially for rattan canes, which can reduce the cane value and limit cane utilization to a large extent. In this study, the dimensional stability and strength of *P. pierreana* canes were effectively improved *via* impregnation treatment with a new water-soluble melamine-urea-formaldehyde (MUF) resin. The MUF resin was modified with low-molecular-weight polyethylene glycol (PEG) and marked as PMUF. This new resin modification technique may promote the exploitation and utilization of inferior rattan canes.

EXPERIMENTAL

Materials

Plectocomia pierreana canes were selected for this study. The diameter and internode length were 22 to 37 mm and 21 to 44 cm, respectively. Samples without nodes were cut from the canes and numbered in sequence; each 12 internodes composed a sampling unit. The first 9 internodes were prepared for the L_9 (3^4) orthogonal test of PMUF resin, the tenth for the control test of MUF resin, the eleventh for untreated canes, and the twelfth for the verification test. Each test had 10 repetitions. Based on the preliminary experiments, the samples were processed into the following sizes for property testing: 20 mm × 10 mm × 10 mm for density, anti-swelling efficiency, and repellency of water absorption; 160 mm × 10 mm × 10 mm for MOE, MOR, and impact toughness; and 30 mm × 10 mm × 10 mm for compressive modulus and strength.

Methods

Experiment design

To obtain the optimum PMUF resin, an orthogonal test $L_9(3^4)$ was designed with 4 factors and 3 levels: PEG molecular weight (200, 400, and 600), marked as A1, A2, and A3; PEG/melamine mole ratio (0.10, 0.20 and 0.40), marked B1, B2, and B3; resin synthetic method (stepwise and blending synthesis), marked C1 and C2; and impregnation concentration (10%, 20%, and 30%), marked D1, D2, and D3. The properties of PMUF and MUF resin-treated canes were compared.

PMUF resin synthesis

First, formaldehyde and melamine were added into a reactor, and the mixture was adjusted to a pH level of 9 and heated to 85 °C for 40 min. Second, PEG was added and reacted at 85 °C for 60 min. Third, a partial portion of urea was added and reacted at 70 °C with a pH level of 11 for 60 min. Then, the remaining urea was slowly added and reacted at 65 °C and pH 9 for 10 min, after which hydrochloric acid was used to adjust the pH of the reactant to approximately 7.5, and the water soluble ratio of the reactant was monitored every 5 min until the ratio reaches 6. Here, the reactant was rapidly cooled, and the stepwise-synthesized PMUF resin was prepared. Finally its pH, solid content, viscosity, and stability were determined and the findings are given in Table 1. The MUF resin synthetic process was the same as the aforementioned, without PEG addition. Blending synthesis corresponded to directly blending PEG with MUF resin. The mole ratio of melamine/urea/formaldehyde was 1: 1.2: 2.3.

Table 1. Properties of PMUF and MUF Resins

PMUF	Solid content (%)	Viscosity (mPa·s)	pH	Stability at 25℃ (day)
1	56.76	16.2	7.5-8.0	30
2	57.12	20.3	7.5-8.0	25
3	58.06	30.3	7.5-8.0	28
4	56.51	24.9	7.5-8.0	40
5	59.38	38.1	7.5-8.0	35
6	65.89	32.3	7.5-8.0	60
7	59.37	35.5	7.5-8.0	60
8	64.48	51.9	7.5-8.0	60
9	68.91	51.5	7.5-8.0	30
MUF	53.21	15.2	7.5-8.0	25

Impregnation treatment

First, the oven-dried samples were placed into an impregnation chamber. Second, the chamber was vacuumed to -0.09 MPa for 30 min. Third, the impregnation solution was added. Thereafter, a positive pressure about 0.6 MPa was applied for 4 h. Then the samples were taken out and cleared. After being air dried for many days, the canes were oven dried. Finally, all the canes were conditioned at 20 °C and 65% RH.

Properties measurement

The density was determined using the water displacement method. The weights and dimensions of the oven-dried canes were measured, both before and after soaking in 2.5 cm of water for 24 h, in order to determine the repellency of water absorption (RWA) and anti-swelling efficiency (ASE), respectively (Chris and Frederic 2008; Norul 2011). The three-point-bending properties were tested with an Instron 5582 (USA) device at a load speed of 10 mm/min over a span of 120 mm. The compressive properties were tested at a load speed of 5 mm/min. The impact toughness test was performed using an Impact tester JB-300B (Jinan Shijin, China). A range analysis of orthogonal test results was carried out to analyze the effects of PEG molecular weight, PEG/melamine (*i.e.*, P/M) mole ratio, resin synthetic method, and solution concentration on resin-treated canes.

SEM characterization

Cubical blocks of size 5×5×2 mm were cut out from treated and untreated rattan cane samples. The blocks were then ion-sputter coated with gold (Au) and observed with a scanning electron microscope (JSM-5500LV, Japan) at an accelerating voltage of 15KV.

RESULTS AND DISCUSSION

Density

All the air-dry densities for canes modified with PMUF or MUF were increased significantly; however, the increase varied greatly, ranging from 19.0% to 132.3% (Table 1). As can be seen from Fig. 1, the density was hardly affected by the resin synthetic method, but it was influenced by the other three factors, especially the solution concentration. The density increased greatly as the solution concentration increased from 10% to 30%. The effects of the PEG molecular weight (PEG) and P/M mole ratio (P/M) on density were not especially strong, and the density reached its maximum value at P/M of 0.1 and PEG-200.

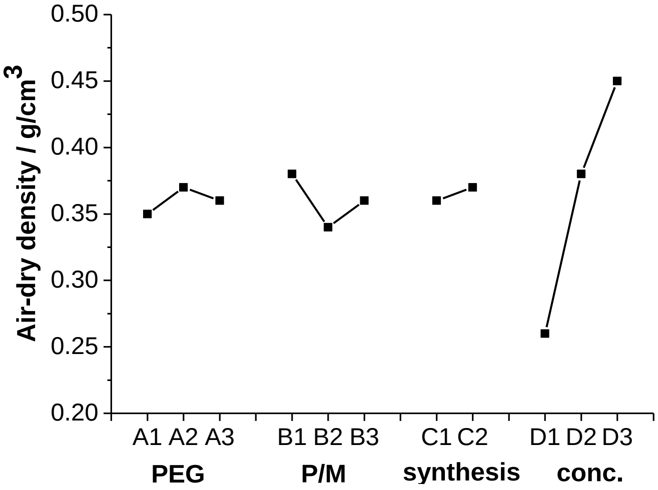

Fig. 1. Effect of the four factors on the air-dry density of PMUF modified canes

Dimensional Stability

Cane anti-swelling efficiency (ASE) and repellency of water absorption (RWA) were closely related to the dimensional stability, as higher ASE and RWA equated to more stable cane products. As shown in Table 2, compared with untreated canes, the PMUF and MUF modified canes tended to have lower volume swelling (VS) and water absorption (WA). The PMUF-modified canes showed much higher ASE and RWA, with an average value of 64.19% and 42.71%, respectively. It was found that the dimensional stability differences between PMUF and MUF treated canes were mainly caused by PEG. This was consistent with the previous report that the WA and thickness swelling of wood-polymer composites decreased significantly after PEG treatment (Luo *et al.* 2012). It was concluded that resin modified with a low molecular weight PEG could easily penetrate into cane cell walls and act as bulking chemicals; thus it became deposited in the cell voids and was able to keep treated samples in a swollen state and reduce the water holding capacity (Chen *et al.* 1995; Luo *et al.* 2012).

Table 2. Dimensional Stability of Resin Modified and Untreated Canes

PMUF	Resin loading (%)	WA (%)	VS (%)	RWA (%)	ASE (%)	ADD (g•cm^{-3})
1	25.56	155.50	4.16	25.46	60.39	0.25
2	28.24	105.77	2.95	49.29	71.95	0.35
3	32.17	84.24	2.96	59.62	71.79	0.45
4	43.29	81.11	3.81	61.12	63.73	0.48
5	46.60	152.51	4.68	26.89	55.38	0.27
6	37.28	125.84	1.43	39.67	86.36	0.37
7	34.11	91.57	5.60	56.10	46.63	0.41
8	36.72	100.45	3.63	51.85	65.45	0.41
9	41.06	178.58	4.61	14.39	56.06	0.27
MUF	43.43	181.26	6.12	13.11	41.71	0.41
untreated	-	208.60	10.50	-	-	0.21
Note: WA- water absorption, VS- volume swelling, ADD - air-dry density (g/cm^3).						

Bending Properties

As shown in Table 3, the MOE and MOR of both MUF and PMUF treated canes improved. Compared with the MUF modified canes, the PMUF modified canes had greater increase in MOE and MOR, with an average of 47.96% and 43.31%, respectively. As can be seen from Fig. 2, the MOE of PMUF modified canes increased significantly with the increasing PEG molecular weight and solution concentration, while no significant effect was observed when the resin synthetic method or P/M ratio was varied in this study. The results were different for the MOR, which was greatly influenced by the four factors and reached its maximum at PEG-600, 0.1 P/M, blending synthesis, and 30% concentration.

Table 3. Mechanical Properties of Resin Modified and Untreated Canes

PMUF	MOE/MPa	MOR/MPa	Compressive modulus/MPa	Compressive strength/MPa	Impact toughness/KJ/m^2
1	695.36	18.53	425.36	7.98	5.22
2	740.81	18.16	437.84	8.26	5.66
3	675.40	17.96	516.54	8.83	5.34
4	829.56	21.19	561.19	10.30	4.25
5	680.38	16.25	501.19	8.42	4.78
6	875.34	15.69	419.85	8.43	3.86
7	826.62	17.89	742.92	11.74	3.24
8	953.01	18.27	572.72	10.41	2.87
9	796.28	19.27	439.10	8.13	2.59
MUF	671.59	15.32	540.00	10.24	2.23
untreated	550.24	12.74	366.65	6.23	5.97

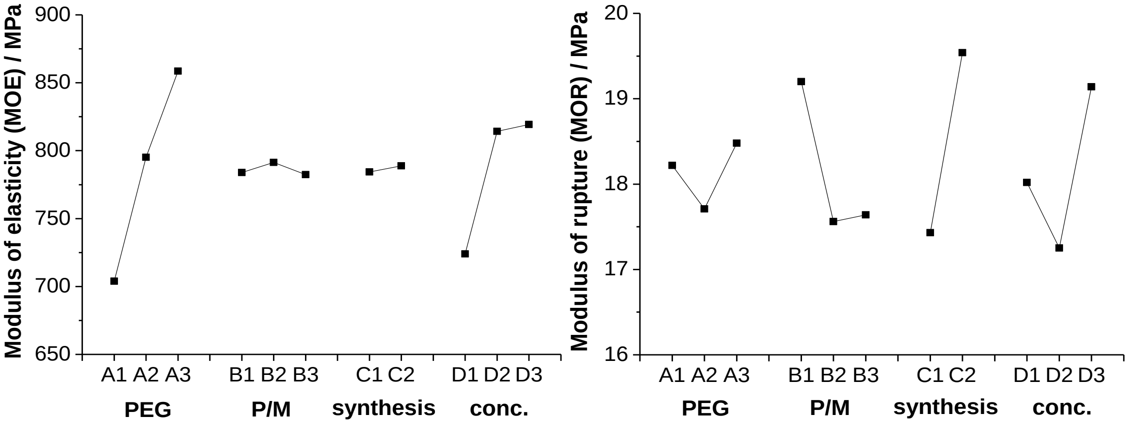

Fig. 2. Effect of four factors on the bending properties of PMUF modified canes

The typical bending stress-strain curves of different resin modified canes and untreated canes are depicted in Fig. 3. Compared with untreated canes, resin modified canes had a shorter curve and a steeper slope. The steeper curve indicated that the ability of the resin-modified cane to resist bending deformation and rupture increased greatly. The shorter curve suggested less bending strain and plastic deformation before rupture. Materials that sustained substantial plastic deformation before rupture are termed ductile, while materials with minimal plastic deformation before rupture are termed brittle (Andrew 2001). The resin treated canes typically cracked at lower amounts of bending deflection or deformation, meaning that canes with resin modifications tended to be more brittle. Compared with MUF modified canes, the PMUF modified canes had much higher and longer curves. It was found that PEG modification of MUF resin could make its impregnated canes strong and flexible. Furthermore, the molecular weight of PEG had a great effect on the cane bending performance. As the PEG molecular weight increased from 200 to 600, the cane bending strength increased and its flexibility decreased. The low molecular weight PEG modification could effectively reduce the MUF resin's brittle effect.

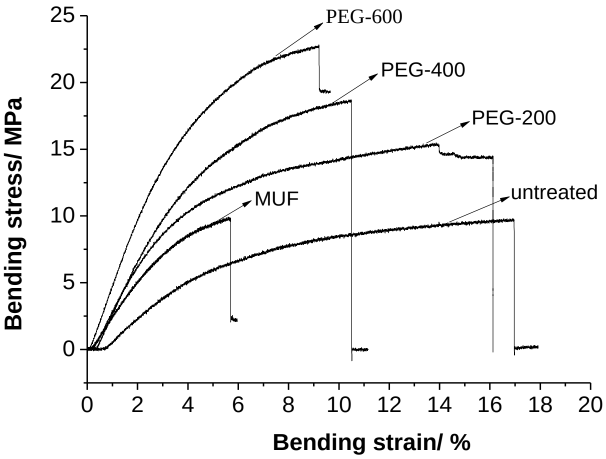

Fig. 3. Bending performance of the canes impregnated with MUF modified with different molecular weight PEG

Compressive Properties

The compressive properties of all resin treated canes was improved (Table 3). The increase in the compressive modulus and strength of PMUF modified canes ranged from 16.01% to 102.92% and from 19.26% to 88.44%, respectively. Some PMUF modified canes had lower values for the compressive modulus and strength compared with MUF modified canes. This might be due to the higher relative resin loading for MUF modified canes (Table 2), which indicated polymers cured in canes could resist pressure. On the other hand, PEG itself did not affect the strengthening property of the cane, and some researchers even found it had negative effect on the mechanical properties (Bardet *et al.* 2007). Bjurhager *et al.* (2010) impregnated wood with PEG-600, and the results showed that the radial compressive MOR and MOE for the treated samples were reduced by 50%. Luo *et al.* (2012) found that the flexural MOR of wood-polymer composites decreased sharply after PEG modification. The compressive modulus and strength were influenced by the four factors in a similar manner (Fig. 4). Additionally, they both increased with increasing PEG molecular weight and solution concentration, as well as decreasing P/M. Higher values were obtained when PMUF resin synthesis was stepwise.

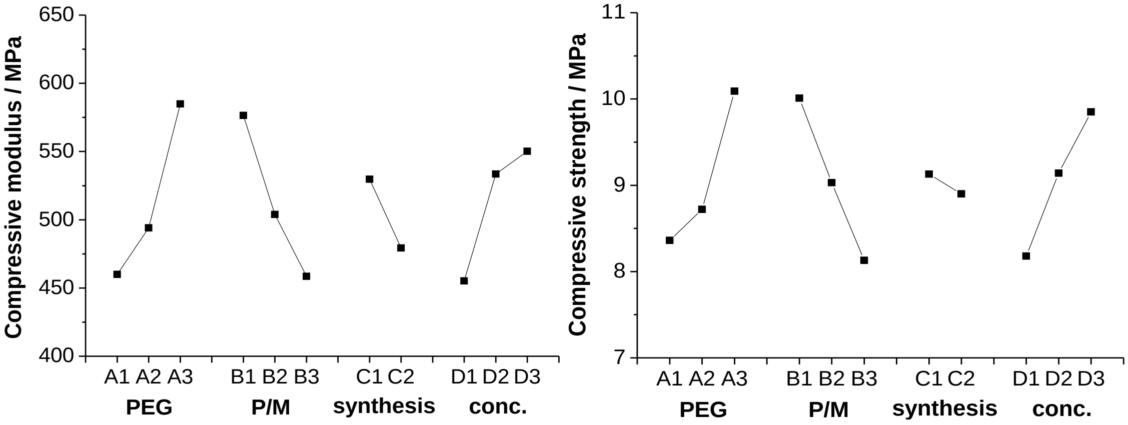

Fig. 4. Effect of four factors on the compressive properties of PMUF modified canes

Impact Toughness

The impact toughness of all resin-modified canes was decreased (Table 3). The MUF modification reduced the toughness by 62.65%, and the PMUF modification reduced it by a minimum of 5.19% and a maximum of 56.62%. In this study, the average impact toughness of the untreated canes was 5.97 KJ/m^2, and the figure was 5.66 KJ/m^2 for canes modified with PEG-200. It was inferred that PEG with low molecular weight could effectively decrease the resin brittleness, further reducing the toughness loss of resin-modified canes. It was discovered that the hydroxyls of PEG could react with the hydroxymethyls in the two triazine rings through dehydration condensation, and form a more flexible bi-triazine ring structure. Then, the bi-triazine rings became compounded with formaldehyde to generate cross-linked MUF resin. Because the partial methylenes binding triazine rings were substituted by PEG, which enlarged the space between triazine rings, and ether and ethylidene bonds occurred during the reaction, the resin flexibility was improved (Ma 1999).

The cane impact toughness was most influenced by the molecular weight of the PEG (Fig. 5). A linear reduction was observed as the molecular weight of PEG increased from 200 to 600. The PMUF resin with PEG-200 treated canes resulted in the highest impact toughness. The impact toughness was also strongly affected by P/M, and reached its maximum when the P/M equals 0.2. Meanwhile, the effects of the solution concentration and synthetic method were minor.

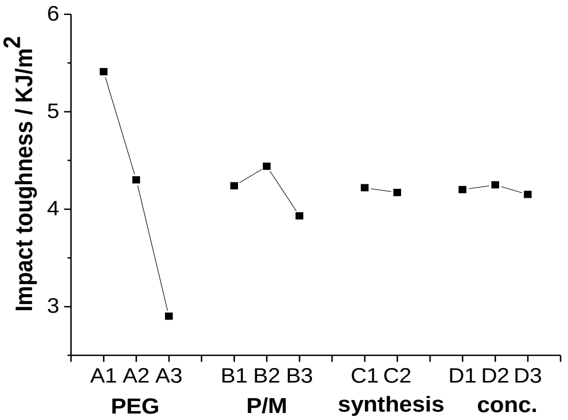

Fig. 5. Effect of four factors on impact toughness of PMUF modified canes

Based on the comprehensive balance between strength and toughness, the optimum PMUF was prepared at PEG-400, 30% concentration, P/M of 0.1, and stepwise resin synthesis. After the cane was treated with the optimum PMUF, its ASE reached 65.51%, the density increased from 0.21 g/cm^3 to 0.43 g/cm^3, the MOR increased from 36.84 MPa to 86.80 MPa, the MOE increased from 640.24 MPa to 1466.19 MPa, and the compressive modulus and strength increased from 925.86 MPa to 1796.30 MPa and from 20.27 MPa to 41.80 MPa, respectively. Its impact toughness experienced only a slight decrease of 6.85%, which was acceptable in practical application. The strength of *P. pierreana* canes were far below commercial *Daemonorops margaritae* canes (Wang *et al.* 2011). With the optimal PMUF resin modification, the strength properties of treated *P. pierreana* canes could exceed those of commercial *D. margaritae* canes. Thus the unutilized *P. pierreana* rattan cane could be exploited as a commercial rattan cane species through PMUF resin modification.

SEM Analysis

The surface morphologies of untreated and optimum PMUF-treated canes were analyzed by SEM. As can be seen from Fig. 6a and 6b, the untreated cane had clean and neat cell walls and cell lumens. However, for PMUF treated cane, the metaxylem vessels, protoxylem vessels, and parenchyma cells were filled with the resin. Furthermore, the untreated cane cell wall surfaces contained a large amount of voids and pits (Fig. 6c), while the surface of PMUF-treated cane were quite smooth, the pits and voids were completely covered with the resin (Fig. 6d). SEM confirmed the presence of PMUF in cane cells, and the resin was uniformly distributed in vessels and parenchyma cells.

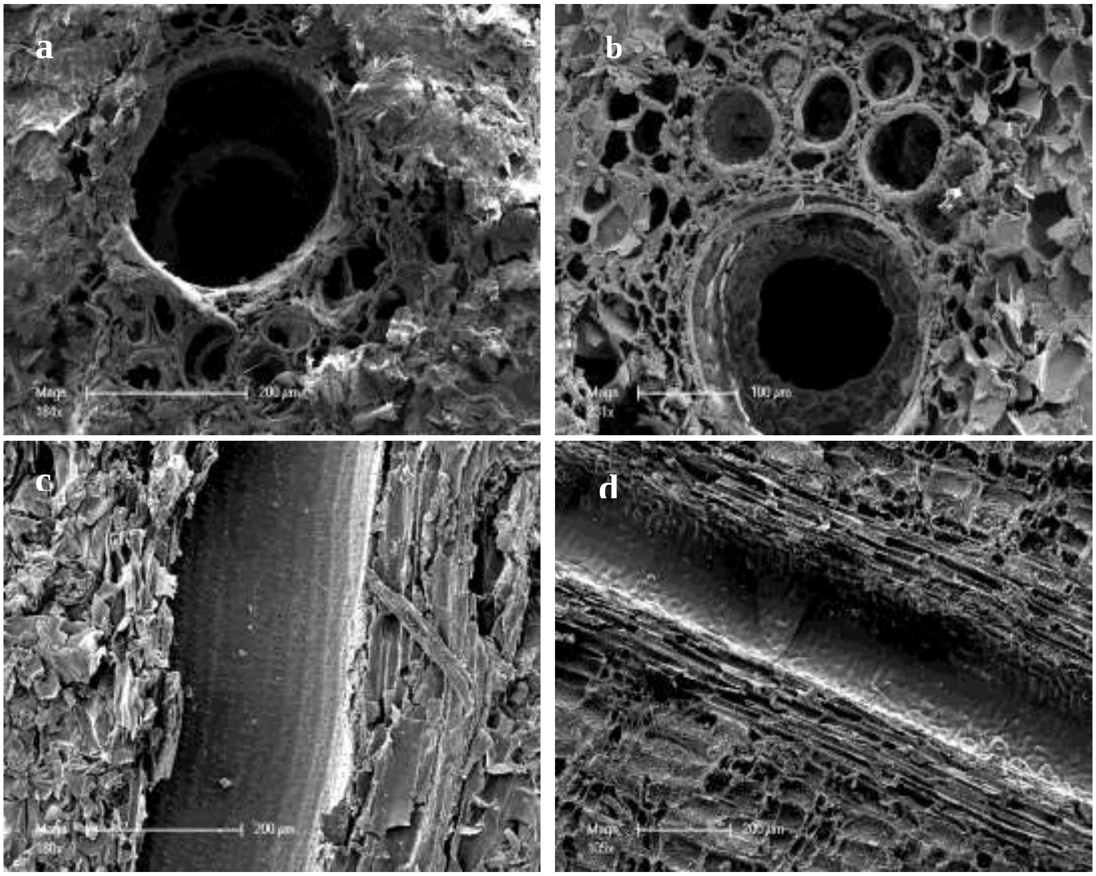

Fig. 6. SEM observation of untreated and optimum PMUF-treated canes: (a) transection of untreated cane, (b) transection of modified cane, (c) radial section of untreated cane, (d) radial section of modified cane

CONCLUSIONS

1. This study investigated the physical and mechanical properties of PMUF and MUF modified *P. pierreana* canes. The effects of PEG on the properties of resin-treated canes were also considered. Results showed that the dimensional stability, density, and mechanical properties except for impact toughness all improved greatly with resin modification.
2. Compared with MUF modified canes, PMUF modified canes showed much higher dimensional stability, MOE, MOR, and impact toughness. The canes modified with PEG-200 had the maximum impact toughness among all of the modification groups, which was very close to that of control samples. It was found during the analysis that PEG was effective at improving dimensional stability and reducing the decrease in impact toughness of resin-treated canes.
3. Strengthened *P. pierreana* canes, with high dimensional stability and good toughness performance could be obtained by PMUF impregnation modification with the

conditions of: PEG-400, P/M mole ratio of 0.1, resin step-wise synthesis, and 30% solution. With the application of the modification technique found in this study, it may be possible to promote the exploitation and utilization of inferior rattan species like *P. pierreana* canes.

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