EFFECTS OF POLYMETHYL METHACRYLATE ON PROPERTIES OF MANAU AND DOK CANES

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NORUL HISHAM, H. & ANWAR, U. M. K. 2005. **Effects of polymethyl methacrylate on properties of manau and dok canes**. Manau (*Calamus manan*) and dok (*C. ornatus*) canes from three different diameter ranges, namely, 25 to 29 mm, 30 to 34 mm and 35 to 39 mm were impregnated with polymethyl methacrylate solution at 20% concentration. Impregnation process was conducted by applying pressure of 20 and 35 min including 5 min vacuum. The pressure and vacuum used were 9 kg cm^{-3} and 700 mmHg respectively. One set from 35 min impregnated samples were oven dried for a further one week to produce thermally-modified samples. Properties of polymer loading, physical (water absorption and antiswelling efficiency), mechanical (static bending, compression and shear) and durability against white rot fungus were measured with the effects of species, cane diameter and impregnation period. This study found that polymer loading was influenced by species, cane diameter and impregnation period. Performance of physical and mechanical properties in modified cane were also dependent to polymer loading. Greater polymer loading in dok significantly increased most of its mechanical properties but this was not observed in manau. However, lower polymer loading in manau had greater physical properties than dok. Untreated dok was more durable than manau. The percentage weight loss following decay of modified cane was significantly reduced with higher polymer loading, which was obtained by longer impregnation period. Thermally-modified canes had lower physical properties than non-thermally-modified samples.

Key words: Cane – physical properties – mechanical properties – durability

NORUL HISHAM, H. & ANWAR, U. M. K. 2005. **Kesan polimetil metakrilat terhadap sifat-sifat rotan manau dan dok**. Rotan-rotan manau (*Calamus manan*) dan dok (*C. ornatus*) daripada tiga julat diameter berbeza iaitu 25–29 mm, 30–34 mm dan 35–39 mm telah diimpregnasi dengan larutan polimetil metakrilat berkepekatan 20%. Proses impregnasi dilakukan menggunakan tekanan selama 20 minit dan 35 minit termasuk 5 minit vakum. Tekanan dan vakum yang digunakan masing-masing ialah 9 kg cm^{-3} dan 700 mmHg. Satu set sampel yang diimpregnasi selama 35 minit dikering lagi dalam ketuhar selama satu minggu untuk membentuk sampel rotan terawat haba. Sifat muatan polimer, sifat fizikal (penyerapan air dan kecekapan tahan kembang), mekanik (lentur statik, mampatan dan ricihan) serta ketahanan daripada kulat pereput putih diukur mengikut spesies, diameter rotan dan tempoh impregnasi. Kajian ini mendapati muatan polimer dipengaruhi oleh spesies, diameter rotan dan tempoh impregnasi. Prestasi sifat-sifat fizikal dan mekanik bagi rotan terubah suai bergantung pada muatan polimernya. Muatan polimer yang tinggi pada rotan dok meningkatkan kebanyakan sifat mekaniknya. Bagaimanapun, ini tidak diperhatikan pada rotan manau. Namun muatan polimer yang rendah pada rotan manau menunjukkan sifat-sifat fizikal yang

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lebih baik daripada rotan dok. Rotan dok daripada sampel kawalan lebih tahan daripada rotan manau. Peratusan kehilangan berat sampel yang dimakan kulat bagi rotan terubah suai berkurangan dengan ketara mengikut peningkatan muatan polimer. Rotan terawat haba mempunyai sifat fizikal yang rendah berbanding sampel tidak terawat haba.

Introduction

Natural beauty and flexibility make rattan a unique material for furniture design application. In many situations, it is unnecessary to improve the cane but better service could be acquired if canes are more dimensionally stable, have greater strength, and are resistant against fungi.

Monomer impregnation in wood followed by *in situ* polymerization has been reported to enhance dimensional stability, hardness, mechanical strength and resistance to fungi and weathering (Kumar 1994, Schneider 1994). However, some monomers do not react or are only partially cured during polymerization process (Schneider 1994). Many monomers also do not penetrate cell walls or do not completely fill voids in the wood after polymerization (Ellis 1994, Zhang *et al.* 2005). This will cause the wood to have voids after treatment, i.e. when the polymer has shrunk.

Properties of Malaysian rattan have been documented (Weiner & Liese 1988, Ani & Lim 1990, Abd. Latif *et al.* 1997, Roszaini 2001). However, not much work has been conducted on chemical modification of cane. Wan Tarmeze *et al.* (1993) investigated the properties of debarked cane modified with phenolic resin. The authors observed that physical and mechanical properties of the cane were greatly improved when higher solid content of the resin was used.

Therefore, in this study, manau (*Calamus manan*) and dok (*C. ornatus*) impregnated with polymethyl methacrylate by solvent exchange process, were examined for their physical, mechanical and durability properties. Improvement of these properties will benefit local furniture industries in terms of development of new products.

Materials and methods

Impregnation procedures

Manau and dok canes from three different diameter ranges, namely, 25 to 29 mm, 30 to 34 mm and 35 to 39 mm were obtained from a local rattan supplier. These canes had been oil cured for 20 to 30 min as common practice in the industry. Defect-free internode sections were trimmed into 20 cm lengths and oven dried to moisture content of between 10 and 12%. Polymethyl methacrylate (density 0.95) of industrial grade was obtained from a local supplier. The solution (20:80 w/w) was prepared by dilution with xylene. The canes were impregnated using vacuum and pressure process of 700 mmHg and 9 kg cm^{-3} respectively. Pressure was applied for 20 and 35 min including 5 min vacuum, separately.

The impregnated canes were then oven dried at 50 °C to constant weight. One set of the 35 min impregnated samples were oven dried for a further one week to produce thermally-modified samples. Polymer loading in samples was measured by subtracting oven dry weight prior to treatment from those following treatment and was expressed as percentage of initial oven dry weight.

Preparation of specimens for testing

Modified cane was cut into 25, 75 and 150 mm lengths for analysis of physical (antiswelling efficiency and water absorption), compression and bending tests respectively. Specimens measuring 30 × 10 × 5 mm were prepared for decay resistance test. Untreated cane was cut to the same dimension as the test specimens.

Antiswelling efficiency and water absorption

Antiswelling efficiency was determined by measuring the increase in saturated volume of treated and untreated specimens. After being weighed and measured for volume, specimens were submerged 15 cm below the surface of distilled water for 24 hours. Specimens were then removed from the water, wiped, weighed and measured for water-saturated volume according to Rowel *et al.* (1986). The percentages of volumetric swelling coefficients were calculated using the formula by Stamm (1964):

$$S\ (\%) = [(V_w - V_d)/\ V_d] \times 100$$

where

V_w = volume of water-saturated cane

V_d = volume of dry cane

The percentage of swelling (ASE) was calculated from the wet and oven dried volumes of treated and untreated samples according to:

$$ASE\ (\%) = [(S_m - S_c)/S_c] \times 100$$

where

S_m = volumetric swelling coefficient of modified specimens

S_c= volumetric swelling coefficient of unmodified specimens

Water absorption (WA) of untreated and modified samples was measured as an index of bulking efficiency from initial and final wet weights after water saturation using the following formula:

$$WA = [W_f - W_i/W_i] \times 100$$

where

W_f = wet weight of specimen after saturation with water

W_i = initial dry weight

Mechanical properties

Bending, compression and shear strength were measured using a Shimadzu Universal Testing Machine. The crosshead speed of 6.6 mm min^{-1} was used for bending and compression, and 0.6 mm min^{-1} for shear.

Decay resistance

Specimens were oven dried at 100 °C, weighed and sterilized with propylene oxide for three days prior to exposure to white rot (*Coriolus versicolor*) growing on 4% malt extract agar media in Petri dishes. The Petri dishes were then incubated at 22 °C for eight weeks. At the end of the incubation period, adhering mycelium was removed and the specimens were dried and weighed. Durability was determined by assessing percentage weight loss.

Results and discussion

The mean for polymer loading, physical properties (antiswelling efficiency and water absorption), mechanical properties (static bending, compression and shear), and percentage weight loss following decay are shown in Tables 1 and 2. In general, the properties were influenced by species, diameters and impregnation period.

Polymer loading

Dok significantly took up more polymer than manau as shown by the greater polymer loading from both 20 and 35 min impregnation period. Average values for polymer loading of dok and manau canes were 46.5 and 30.3% respectively (Table 1). This indicated that dok was more permeable than manau. However, this result contradicts observation made by Zaidon and Petty (1998). The authors mentioned that lower permeability of dok was probably due to the presence of gum in vessels, as non-oil-cured rattans were used. Oil curing process for rattan helps remove moisture, waxy material, resin and gum, improves colour quality, texture and flexibility, and, to some extent, prevents fungal and insect attacks (Silitonga 1989). Impregnation period of 35 min gave higher polymer loading in cane compared with 20 min. The average loading values for the former period were 34.1 and 57.7% in manau and dok respectively (Table 1).

The biggest diameter cane took up more polymer than canes with smaller diameters, which indicated its higher permeability (Table 2). Higher loading in dok having the biggest diameter probably resulted from its lower density and greater void volume. Density of manau is higher than dok (Zaidon *et al.* 1996). Also bigger cane has lower density than smaller cane as rattan matures from the basal towards the top portions (Bhat 1991). Unlike bamboo, most large diameter rattan, including manau and dok, was tapered from the top towards the basal portions. In wood, permeability is also influenced by species and density (Nicholas & Siau 1973).

Table 1 Mean properties of modified and untreated canes

Property	Impregnation period	Species		Significance (between species)
		Manau	Dok	
Polymer loading (%)	Control	-	-	
	20	23.7[a]	31.5[a]	
	35	34.1[b]	57.7[c]	
	35T	33.2[b]	50.2[b]	
	Mean	30.3	46.5	***
Water absorption (%)	Control	59.5[c]	99.3[d]	
	20	26.6[ab]	50.5[b]	
	35	21.4[a]	38.9[a]	
	35T	30.6[b]	65.7[c]	
	Mean	34.5	63.6	***
Antiswelling efficiency (%)	Control	-	-	
	20	53.7[a]	48.6[a]	
	35	66.0[b]	61.4[b]	
	35T	45.9[c]	44.0[a]	
	Mean	55.2[b]	51.3	**
Static bending Modulus of rupture (MOR) (MPa)	Control	87.4[a]	43.9[a]	
	20	106.7[a]	60.1[c]	
	35	101.0[a]	50.5[ab]	
	35T	100.1[a]	53.0[bc]	
	Mean	98.8	51.9	***
Static bending Modulus of elasticity (MOE) (MPa)	Control	116.9[a]	43.6[a]	
	20	138.7[a]	74.7[b]	
	35	125.1[a]	73.7[b]	
	35T	138.6[a]	78.7[b]	
	Mean	129.8	67.7	***
Compression (MPa)	Control	28.9[a]	16.2[a]	
	20	38.1[b]	19.4[b]	
	35	39.2[b]	22.7[c]	
	35T	37.5[b]	20.1[b]	
	Mean	35.9	19.6	***
Shear (MPa)	Control	8.5[a]	6.2[ab]	
	20	10.0[bc]	7.0[b]	
	35	10.3[c]	6.1[a]	
	35T	9.0[ab]	6.9[b]	
	Mean	9.5	6.6	***
Weight loss following decay (%)	Control	28.5[c]	16.9[c]	
	20	14.1[ab]	6.6[a]	
	35	10.3[a]	5.3[a]	
	35T	18.1[b]	9.3[b]	
	Mean	17.8	9.5	***

** = $p < 0.05$ and *** = $p < 0.01$
For each property, values followed by the same letter(s) in the same column are not significantly different at the 0.05 probability level.
T = thermally-modified cane

Table 2 Duncan's multiple range test on effects of diameter and impregnation period to properties of modified and untreated canes

Property	Diameter (mm)	Species	
		Manau	Dok
Polymer loading (%)	25 to 29	28.5[a]	47.1[ab]
	30 to 34	28.4[a]	41.7[a]
	35 to 39	34.1[b]	51.1[b]
Water absorption (%)	25 to 29	34.7[a]	65.0[b]
	30 to 34	35.4[a]	63.1[ab]
	35 to 39	34.6[a]	59.7[a]
Antiswelling efficiency (%)	25 to 29	58.7[a]	39.2[a]
	30 to 34	56.1[a]	55.9[b]
Static bending	35 to 39	40.7[a]	59.9[b]
(MOR) (MPa)	25 to 29	102.2[a]	52.1[a]
	30 to 34	100.5[a]	51.9[a]
	35 to 39	90.6[a]	52.0[a]
Static bending	25 to 29	163.1[a]	91.8[a]
(MOE) (MPa)	30 to 34	122.9[b]	58.5[b]
	35 to 39	103.4[b]	54.3[b]
Compression (MPa)	25 to 29	39.4[b]	21.1[a]
	30 to 34	34.4[a]	18.9[b]
	35 to 39	34.0[a]	19.2[b]
Shear (MPa)	25 to 29	11.2[a]	7.5[b]
	30 to 34	8.9[b]	6.4[a]
	35 to 39	8.3[b]	5.8[a]
Weight loss (%)	25 to 29	14.4[a]	11.4[b]
	30 to 34	17.1[a]	6.4[a]
	35 to 39	21.8[b]	10.1[b]

For each property, means followed by the same letter(s) in the same column are not significantly different at the 0.05 probability level.

Water absorption and antiswelling efficiency

Untreated manau restricted more water than dok. Average water absorption of untreated manau and dok were 59.5 and 99.3% respectively (Table 1). Higher density of manau probably slowed water uptake during the 24 hours submersion period. Water absorption following modification was reduced with increasing polymer loading resulting from longer impregnation period. Impregnation of 35 min gave lower water uptake than that of 20 min in both manau (21.4%) and dok (38.9%). Cane diameters did not influence water uptake in manau and this could be attributed to the lower polymer loading in this cane (Table 2). However, for dok, the biggest cane had the lowest water uptake.

Similar to water absorption, antiswelling efficiency of manau (55.2%) was significantly higher than dok (51.3%) (Table 1). Highest antiswelling efficiency was observed from impregnated cane at 35 min period for both manau (66.0%) and dok (61.4%). Cane diameters did not influence antiswelling efficiency in manau, but dok with biggest diameter range had greater antiswelling efficiency than those with smaller diameters (Table 2).

Mechanical properties

Untreated manau had higher static bending, compression and shear strengths than dok. The average values for modulus of rupture (MOR), modulus of elasticity (MOE), compression and shear in untreated manau were 87.4, 116.9, 28.9 and 8.5 MPa compared with dok, 43.9, 43.6, 16.2 and 6.2 MPa respectively (Table 1). Polymer impregnation did not improve MOR and MOE in manau. In dok, highest MOR was observed from cane impregnated for 20 min (60.1 MPa). Unlike manau, MOE in modified dok was greater than in the untreated cane. Impregnation period did not influence the MOE in treated manau and dok. However, compression increased with impregnation period in dok but not in manau. This could be caused by the lower polymer loading in manau as an effect of its lower permeability. Modified manau and dok had higher compression than their untreated controls. Highest shear value in manau (10.3 MPa) was obtained from cane impregnated for 35 min while for dok (7.0 Mpa), 20 min.

Cane diameters, for both species, did not influence the MOR values. However, canes with smallest diameter in both species had significantly higher MOE, compression and shear than canes with bigger diameters (Table 2). Untreated wood has lowest compression values due to buckling of relatively thin cell walls; therefore, the addition of polymer as a coating on cell walls thickens them and greatly increases their stability (Siau *et al.* 1968).

Resistance against white rot

Weight loss of 28.5 and 16.9% following decay was observed in untreated manau and dok respectively (Table 1). The higher weight loss in the former indicated that dok was more durable than manau. Oil curing process for manau and dok was not able to protect the canes against white rot. Lowest percentage weight loss was obtained from canes impregnated at 35 min (highest loading) for both manau (10.3%) and dok (5.3%).

Cane diameters of 25–29 mm and 30–34 mm in manau and dok had the lowest percentages weight loss than other bigger diameter canes, despite its lower polymer loading. In wood, lower decay rate in wood polymer composite may be attributed to a reduction in wood hygroscopicity and inhibition of fungal colonization (Yalinkilic *et al.* 1998).

Thermally-modified cane

Thermally-modified cane had lower polymer loading than those from non-thermal, 35 min impregnated samples and this further decreased its physical properties (water absorption and antiswelling efficiency) and durability for both species. Except shear, all mechanical properties of manau were not affected by the thermal process. In thermally-modified dok, increases in MOR and shear were observed compared with the 35 min impregnated dok. However, compression of the modified cane was reduced and no changes in MOE occurred (Table 1).

Conclusions

Polymer loading which indicated cane permeability was dependent on species, cane diameter and impregnation period. Polymer loading was higher in dok than in manau and it was also higher in bigger diameter canes. Impregnation period also influenced loading. Modified manau had greater physical properties compared with modified dok, despite its lower loading. Physical properties of modified cane also differed with cane diameter.

Untreated manau had greater mechanical properties than dok. Mechanical properties of modified cane also differed with species and diameter and they were affected mostly by polymer loading. Untreated dok was more durable than manau and polymer impregnation increased its durability. Thermally-modified cane had lower physical properties and durability than non-thermally-modified sample.

Modified cane with polymer would generate additional production cost. Therefore, only products in selected fields of application are feasible for this process, where extra cost could be coordinated with quality improvement of service life (Liese 1994). Polymer dilution should be processed in a system with good ventilation. Pressure release, which contains gas, should be discharged in container containing water. This procedure will minimize the risks for workers.

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