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Effects of Polymer Impregnation on Properties of Bamboo

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ABSTRACT

This research is targeted to investigate the effects of polymer impregnation on the properties of bamboo. Polymer impregnation can improve adhesion of flattened bamboo and also improve the resistance of polymer-impregnated bamboo to fungi. During the flattening bamboo process, linseed oil was used as a processing aid. Two different kinds of solvents, methanol and ethanol, were used to extract linseed oil. Weights of samples before and after extraction were compared. Ethanol is a better solvent than methanol to extract linseed oil since weight loss is higher. The flattened bamboo samples were adhered together by phenol-formaldehyde (PF) adhesive or polymeric diphenylmethane diisocyanate (MDI) adhesive. The adhesion test was performed in shear mode. Sample extracted with ethanol and adhered by MDI gave a maximum shear stress of 5.84 MPa while samples extracted with methanol and adhered by PF gave only 2.45 MPa. A higher percentage of wood failure was observed in samples with higher adhesion strength. In durability to fungi, a polymer-wood composite was made by impregnation of methyl methacrylate in the wood under vacuum. The composite showed better resistance to fungi, especially, in nodes. Nodes have a lower densities and less effective packing of fibers than internodes. Therefore monomers can diffuse into node and then polymerize. More polymer loading gives better durability to fungi.

Keywords: Flattened bamboo, phenol-formaldehyde adhesive, diphenylmethane diisocyanate adhesive, polymer impregnation

INTRODUCTION

Bamboo is a very fast growing plant with very high strength so it can be used as a structural material. It has higher tensile strength than other wood [1,2]. Its chemical compositions and strength are shown in **Table 1**. Since bamboo has a hollow cylinder shape, it can be flattened by pressing in heated linseed oil [3]. However, flattened bamboo with absorbed linseed oil may not have good adhesion since the oil, a substrate with low surface energy, will often diffuse into the surface and deteriorate adhesion [4]. In this work, the aim is to improve adhesion by removing linseed oil by extraction, before applying the adhesive.

Table 1 Chemical compositions and tensile strength of bamboo and wood [1,2].

	Bamboo	**Wood**
Cellulose (%)	45.3	40-50
Hemi-cellulose (%)	-	20-35
Lignin (%)	25.5	15-35
Polyoses (%)	24.3	-
Extractive (%)	2.6	< 10
Tensile Strength (MPa)	150-520	34-220

There are many types of widely used adhesives in industry. In this work, two types of adhesives were studied and their adhesion strengths were compared.

1. Phenol-Formaldehyde (PF): there are two types of PF adhesives, Novolaks and Resoles. In wood composite industries, resoles in liquid form is well-used. A simple structure of PF is shown in **Figure 1** [5]. PF can have hydrogen bonding and mechanical interlocking with wood [6].

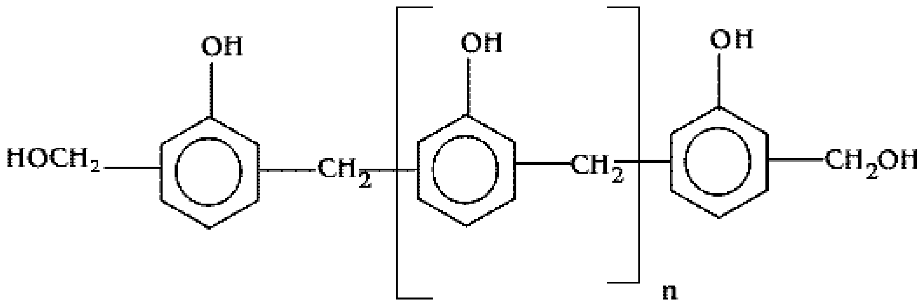

Figure 1 Structure of phenol-formaldehyde (PF) adhesive.

2. Polymeric Diphenylmethane Diisocyanate (MDI) or Isocyanate adhesive. The monomer is a mixture of diisocyanate isomers: 4,4'-MDI, 2,4'-MDI and 2,2'-MDI and its polymer has simple structure as shown in **Figure 2** [7].

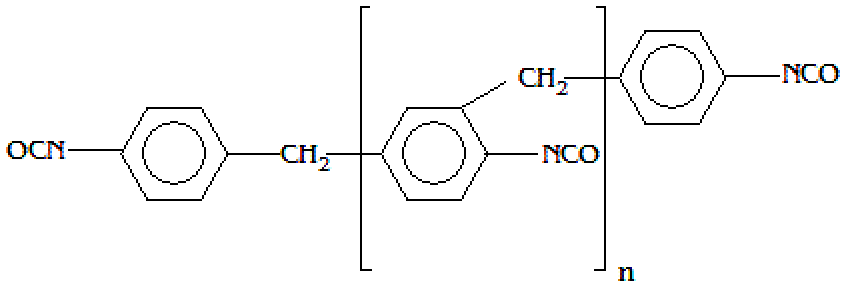

Figure 2 Structure of diphenylmethane diisocyanate (MDI) adhesive.

Cracks take place at the weakest phase/interphase/interface. There are three modes of failure [4]:

1. Interfacial or clean separation that occurs in case of poor adhesion between the adhesive and adherent.
2. Cohesive failure in the adherent that takes place where adhesion is very strong and cohesive strength of the adhesive is higher than that of adherent.
3. Cohesive failure in the adhesive layer that occurs when interfacial strength is very high and cohesive strength of the adherent is high. However, the thermoset adhesive has 3-dimensional network so it has very high cohesive strength.

In the case of poor adhesion, we would see interfacial failure. However, we would see cohesive failure in wood or in the adhesive layer in the case of good adhesion. In many cases, mixed modes could be observed [8].

Wood, a biological material, has low durability to fungi. However, polymer impregnation is one of the methods to make a wood-polymer composite with better mechanical properties and durability [9,10]. In this work, we investigate the effect of polymer impregnation in wood and its resistance to fungi in the nodes and internodes.

MATERIALS AND METHODS

Linseed Oil Extraction

Black-sweet bamboo (*Dendrocalamus asper* Becker) was cut from bamboo plants in Thasala District, Nakhon Si Thammarat. The wood was cut into half-cylinders and polished by a chisel to get a smooth surface. Then it was flattened by putting in heated linseed oil and pressed for suitable time and pressure [3]. The flattened bamboo with adsorbed linseed oil was cut into ~ 2.5 cm x 8.0 cm samples and the samples were weighed. Then the samples were put on filter paper in a soxlet extractor and extracted with either methanol (CH_3OH) or ethanol (C_2H_5OH) to remove the linseed oil. The temperature was adjusted to obtain slow boiling of the solvent. Samples were extracted for 6 h (longer times caused the flattened bamboo to spring back so that samples could not be used for the adhesion test). Weights of 18 - 21 pieces of samples were in range of 5.50 - 7.50 g depending on sample thickness. After extraction, samples were put in the oven at 103 °C for 18 h, and the dry samples were subsequently weighed. The ratio of the weight of the extracted sample compared to the original weight was calculated. Results between using methanol and ethanol as solvents for linseed oil extraction of the flattened bamboo were compared.

Adhesion Strength

Phenol-Formaldehyde adhesive was mixed at a ratio suggested by the manufacturers. An appropriate amount of adhesive was spread on the extracted samples. Two pieces were then pressed together in a compression molding press at 120 - 140 °C for 6 min (cure time). The test method is according to the procedure of ISO standard 6237: 1987 [11].

Samples were conditioned at relative humidity 65 %, 20 °C for 7 days or until the weight of sample was constant. Using a small saw, the top piece was cut at 3.0 cm from the left to the glue line and the bottom piece was also cut at 3.0 cm from the right to have a bonded length of 2.0 cm (sample length is 8.0 cm), as shown in **Figure 3**. Samples were tested by a universal testing machine in shear mode to obtain maximum shear load.

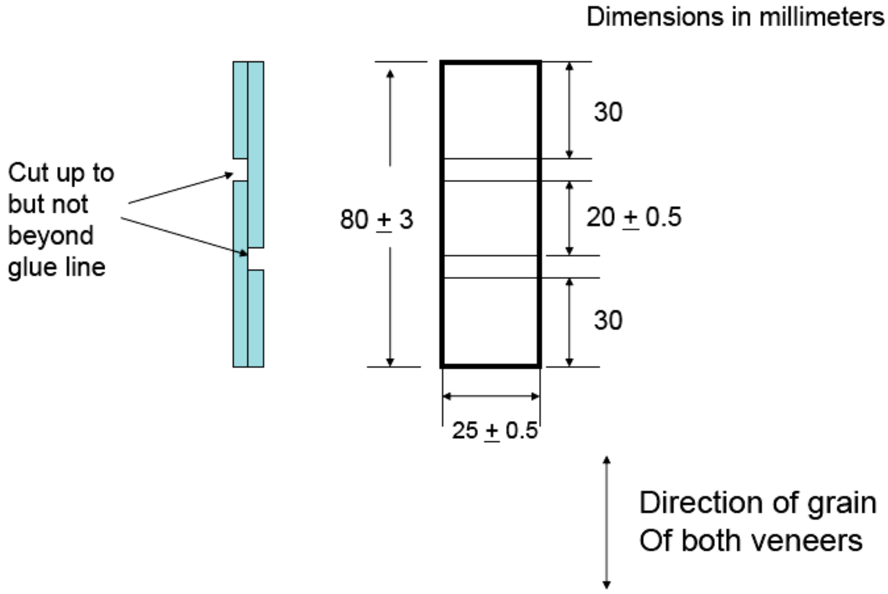

Figure 3 Sample preparation for shear stress.

Polymeric diphenylmethane diisocyanate (MDI) adhesive was used instead of phenol-formaldehyde (PF), and the strengths of PF and MDI adhesive for samples extracted by ethanol or methanol were compared. SAS (Statistic Analysis System) version 6.12 was used to analyze data. Tested specimens were examined to determine the failure mode (interfacial or clean separation, cohesive failure).

Durability of Poly(Methyl Methacrylate)-impregnated Bamboo

Inhibitor in methyl methacrylate (MMA) was removed by solvent extraction about 3 - 4 times until there was no red color in the solvent layer. Then benzoyl peroxide (initiator for polymerization of MMA) was added to MMA at 2 % by weight and stirred to ensure good mixing with MMA. Bamboo pieces were placed in a vacuum vessel, and then the vacuum pump was turned on for at least 5 min until the vacuum gauge read almost 10^{-2} mm Hg. At low pressure, the vacuum pump was turned off, and the mixture of MMA and initiator was added in another glass tube that was connected to the vacuum vessel. The valve was turned on to let the mixture of MMA and initiator into the vacuum vessel containing bamboo pieces. Five minutes were allowed to let wood specimens absorb MMA into their cavities. The MMA-soaked samples were wrapped with aluminum foil. The samples were polymerized in steam for 30 min. Then PMMA-coated samples were unwrapped. Two parts of bamboo were studied: internode and node (**Figure 4**).

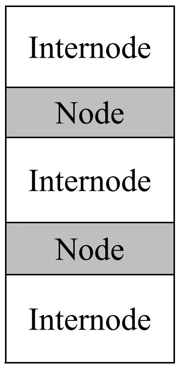

Figure 4 Internodes and nodes of bamboo.

For durability to fungi, samples were put in an incubator at 30 °C, humidity of 70 % and data (number of spores) were collected at 2, 4, 6 and 8 weeks. Fungi spores were determined by putting a sample in 10 ml of 5 % tween-80 solution which was then shaken by a vortex mixer for 2 min. The wood was taken out and the suspended spores were counted by use of a heamacytometer and microscope.

RESULTS AND DISCUSSION

Linseed Oil Extraction

Linseed oil with low liquid surface energy has a tendency to diffuse into the surface in order to decrease the total Gibbs' free energy. Therefore, good adhesion cannot be obtained on oily surfaces. So it is necessary to remove the oil in order to get good adhesion. The ratios of weight after and before extraction were calculated. Results are shown in **Figure 5**.

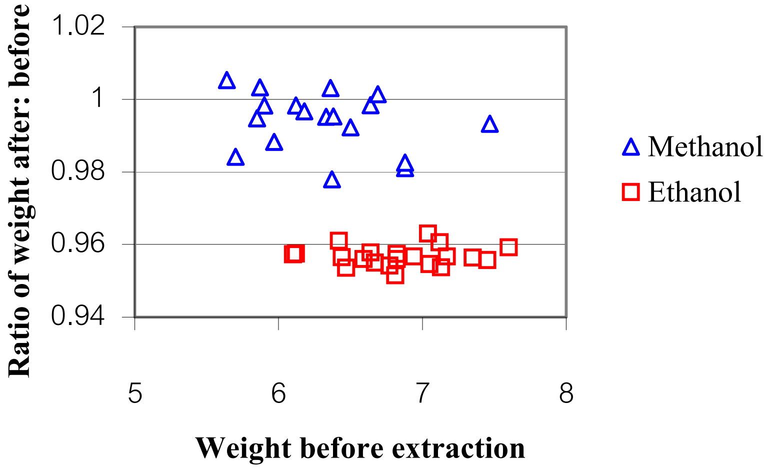

Figure 5 Weight ratios of samples after and before extraction by methanol or ethanol.

For extraction by methanol, the ratio of weight was 0.994 $\pm$ 0.008 or 99.4 $\pm$ 0.8 %, not significantly different ($p>0.05$) from 1.000 or 100 %. The result implies that methanol is not a suitable solvent to extract linseed oil from the wood. However, for extraction by ethanol, the ratio of weight was 0.957 $\pm$ 0.003 or 95.7 $\pm$ 0.3 %. Extraction by ethanol decreases the weight by 4.3 $\pm$ 0.3 %. One can conclude that ethanol is more effective in extracting the linseed oil from the sample. Both methanol and ethanol are polar solvents and exhibit hydrogen bonding.

The reasons why ethanol can extract linseed oil better than methanol are (1) ethanol has a longer nonpolar chain (C_2H_5) than methanol (CH_3), so the longer nonpolar part can extract oil that is a nonpolar liquid, and (2) the boiling point of ethanol is higher than methanol so the sample was extracted at a higher temperature so it is easier to remove the linseed oil. At this point, better adhesion for samples extracted by ethanol is expected.

Adhesion Strength

Methanol and ethanol were used to extract linseed oil from the flattened bamboo. Results of maximum shear stress are shown in **Table 2**. Failure mode is very important to justify if adhesion is good or not. We used an optical microscope to look at the sample surface after failure to see percentage of “wood failure” or “cohesive in wood”.

Table 2 Maximum shear stress (MPa) of samples ($\overline{X} \pm$ S.D.) extracted with methanol and ethanol using Phenol-Formaldehyde (PF) and Polymeric Diphenylmethane Diisocyanate (MDI) or Isocyanate adhesives.

Adhesive		**Max. shear stress (MPa)**	**Wood failure (%)**
Phenol-formaldehyde (PF)	Unextracted	2.22 ± 0.21	14 ± 03
	Methanol	2.45 ± 0.40	26 ± 05
	Ethanol	2.45 ± 0.23	38 ± 12
Polymeric Diphenylmethane Diisocyanate (MDI)	Unextracted	3.83 ± 0.65	20 ± 07
	Methanol	4.88 ± 1.82	33 ± 10
	Ethanol	5.84 ± 0.53	60 ± 08
F		ns	ns
		Ratio	
Strength of MDI: PF	Unextracted	1.72	
	Methanol	1.99	
	Ethanol	2.38	

ns = nonsignificant difference (P>0.05)

It is very obvious that phenol-formaldehyde (PF) is not a good adhesive for our system since maximum shear stresses were quite low, 2.22 - 2.45 MPa. From an average of maximum shear stresses and standard deviation, solvent extraction does not improve adhesion (**Figure 6**). Using an optical microscope to examine specimen surface, wood failure percentage was low (14 ± 3 % for unextracted samples and 38 ± 12 % for samples extracted with ethanol) (**Table 2**).

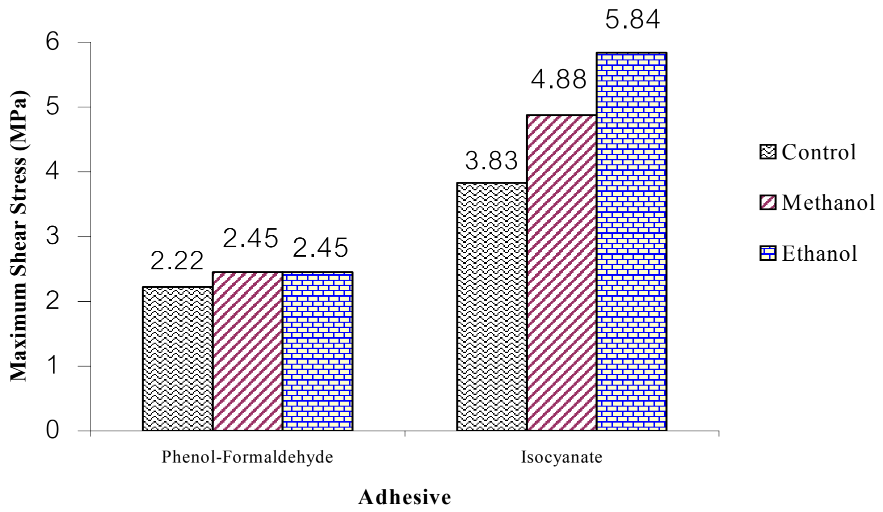

Figure 6 Maximum shear stress of sample bonded by phenol-formaldehyde or isocyanate adhesive.

In order to justify if extraction has any effect on adhesion of PF, we used SAS (Statistic Analysis System) to analyze adhesion strengths. The results show that there is no significant difference ($P>0.05$) in strengths of control, methanol and ethanol extracted samples. However, the isocyanate adhesive is much more effective than PF since the adhesion strengths were 1.72 - 2.38 times than those of phenol-formaldehyde, and wood failure percentages were higher (20 $\pm$ 7 % for unextracted, but 60 $\pm$ 8 % for ethanol extracted) (**Table 2**). For samples without extraction, MDI gave strength 1.72 times that of PF. Adhesion improved greatly in extracted samples. Ratios of strength in MDI: PF are 1.99 for methanol, and 2.38 times for ethanol.

Durability of Poly(Methyl Methacrylate)-Impregnated Bamboo

Durability to fungi of Poly(Methyl Methacrylate)-impregnated bamboo was tested. We studied two parts of bamboo, internodes and nodes. The fungi spore determinations at different incubation times are shown in **Figure 7**.

PMMA coated samples (filled symbols) (**Figure 7**) had lower numbers of spores suggesting better resistance to fungi, especially, nodes (filled squares) that had the lowest number of fungi spores. One can explain that nodes have a lower density or less effective packing of fiber so the monomer can diffuse in it and then polymerize. Since polymer loading in the node is higher, it has a lower number of spores than the control.

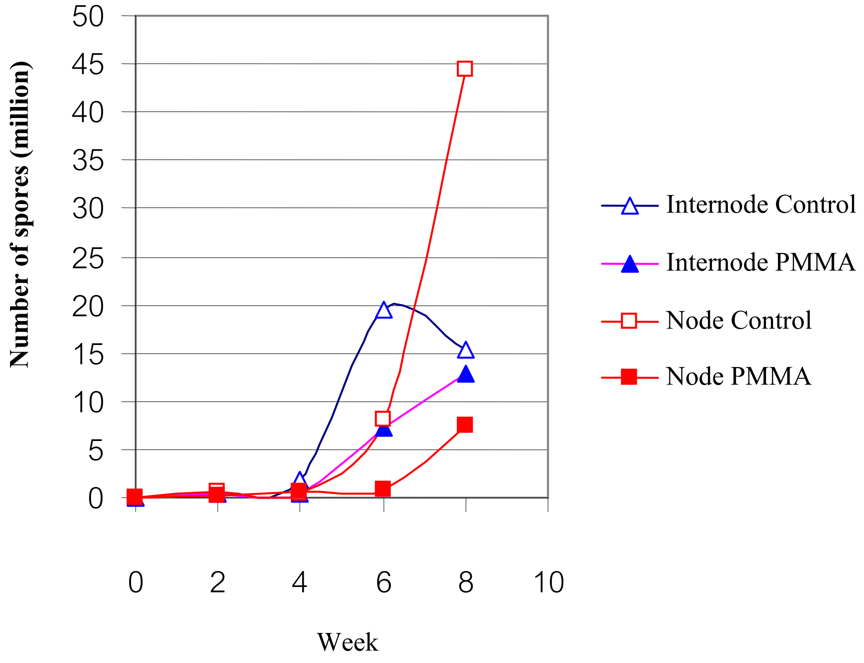

Figure 7 Number of fungi spores in internode and node in control and PMMA-wood composites at various incubation times.

CONCLUSIONS

From this work, some conclusions can be drawn:

1. Ethanol is a better solvent than methanol to extract linseed oil so samples extracted with ethanol have higher weight loss due to higher oil removal.
2. Isocyanate is a better adhesive than Phenol-Formaldehyde in all cases; control, methanol-extracted and ethanol-extracted. The difference in isocyanate adhesion strength is the largest in samples extracted by ethanol.
3. Polymer-impregnated wood has higher durability to fungi.
4. Nodes of bamboo have more cavities or lower densities than internodes. Therefore, polymer loading is higher, resulting in better durability to fungi.

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EFFECTS OF POLYMER IMPREGNATION ON PROPERTIES OF BAMBOO

บทคัดย่อ

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การแทรกซึมของพอลิเมอร์ต่อสมบัติของไม้ไผ่

งานวิจัยนี้มีวัตถุประสงค์ศึกษาผลของการแทรกซึมของพอลิเมอร์ต่อสมบัติของไม้ไผ่ การแทรกซึมของพอลิเมอร์สามารถเพิ่มการติดประสานกันของแผ่นไม้ไผ่คลี่และความคงทนของไม้ไผ่ที่มีพอลิเมอร์แทรกซึมต่อเชื้อรา ในกระบวนการคลี่แผ่นไม้ไผ่ มีการใช้น้ำมันลินสีดช่วย ดังนั้นจึงต้องสกัดน้ำมันออกโดยใช้เมทานอลและเอทานอล น้ำหนักก่อนและหลังการสกัดถูกนำมาเปรียบเทียบ พบว่าเอทานอลทำให้น้ำหนักของตัวอย่างลดลงมากกว่า แสดงถึงประสิทธิภาพในการสกัดน้ำมันออกมา กาว 2 ชนิด ได้แก่ กาวฟีนอลฟอร์มัลดีไฮด์ (PF) และกาวไดฟีนิลมีเทน ไดไอโซไซยาเนต (MDI) ได้นำมาศึกษาเปรียบเทียบในการทดสอบแบบเฉือน พบว่าชิ้นตัวอย่างที่สกัดด้วยเอทานอลและติดด้วยกาว MDI ให้ค่าความแข็งแรงแบบเฉือน 5.84 MPa ในขณะที่ชิ้นตัวอย่างที่สกัดด้วยเมทานอลและติดด้วยกาว PF ให้ค่าเพียง 2.45 MPa ร้อยละของการฉีกขาดในเนื้อไม้พบในชิ้นตัวอย่างที่มีความแข็งแรงสูงกว่า ในการทดสอบความคงทนต่อเชื้อรา ไม้ไผ่ถูกนำไปแช่ในเมทิล เมทาไครเลตในสุญญากาศ แล้วทำการพอลิเมอไรซ์ เพื่อเตรียมวัสดุเชิงประกอบไม้-พอลิเมอร์ ผลการทดลองพบว่า ไม้เชิงประกอบมีความคงทนต่อราสูงขึ้น โดยเฉพาะบริเวณข้อ เพราะเป็นบริเวณที่มีความหนาแน่นต่ำและการจัดเรียงตัวของเส้นใยน้อยกว่าในส่วนของปล้อง ทำให้โมโนเมอร์ซึมเข้าไปได้มากกว่า และมีปริมาณของพอลิเมอร์มากกว่า จึงมีผลให้มีความคงทนต่อราเพิ่มขึ้น

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