Finishing Properties of Bleached and Unbleached Bio-polyurethane Wood Coating

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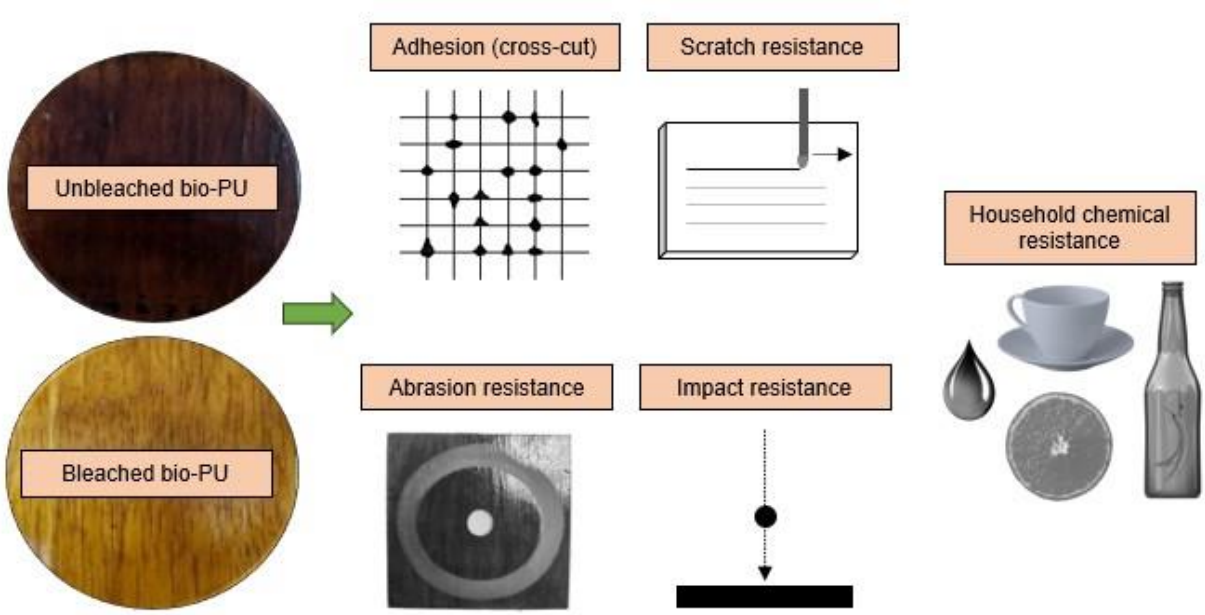
GRAPHICAL ABSTRACT



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To obtain a more appealing wood coating with lighter color, bleaching treatment was employed. Bleached and unbleached bio-polyurethane (PU) coating was prepared using liquefied bamboo and was applied to rubberwood. The coated wood surface was examined for adhesion, scratch, abrasion, impact, and resistance to common household chemicals. The results revealed that the bleaching of liquefied bamboo exerted mixed effects on the finishing properties of the bio-PU coating. Specifically, the surface coated with unbleached bio-PU coating exhibited noticeably higher levels of scratch and impact resistance compared to the surface coated with bleached bio-PU coating. However, both the adhesion and abrasion properties were found to be similar in both cases. Both bleached and unbleached bio-PU coating exhibited similar resistance to various household chemicals, with exception of acetic acid. This research demonstrated a method for producing semi-transparent bio-PU from bamboo biomass for use in wood coating. Bleaching treatment is feasible to produce light-colored coating without significantly affecting the finishing properties of the bio-PU coating.

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Keywords: Wood finishing; Bleaching; Staining; Organic coatings; Bleaching treatment

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INTRODUCTION

Polyurethanes (PU) are highly adaptable substances that find utility in a wide range of polymer applications, encompassing foams, elastomers, sealants, fibres, adhesives, and coatings (Cheumani *et al.* 2015). PU products are renowned for their outstanding adhesion, abrasion resistance, toughness, excellent gloss, colour protection, as well as their high corrosion protection ability and chemical resistance (Olcay *et al.* 2020). The utilisation of PU in the coating industry is on the rise due to its exceptional characteristics, including adhesion, abrasion resistance, toughness, flexibility, and chemical and corrosion resistance

(Jakhmola *et al.* 2024). This has led to its increased application in various sectors such as wood furniture and floorings, the automotive industry, and chemical resistance coatings.

Currently, PU is being synthesized from various biomass sources, which contributes to a goal of renewability. Silva *et al.* (2023) conducted research that involved the utilisation of two types of bio-PU derived from pinewood and *Stipa tenacissima* biomass sources. The bio-PU materials were effectively utilized as eco-friendly ingredients for the creation of bio-based PU coatings on surfaces of carbon steel. Another research investigation was conducted by Gharib *et al.* (2020). They manufactured polyurethane from pyrolysis bio-oil produced from radiata pine wood and reacted it with methylene diphenyl diisocyanate (MDI). The researchers found that gradually adding pyrolytic lignin to MDI overcame the issue of a brittle polymer and made it more suitable for use as a protective coating. Meanwhile, the research conducted by Piao *et al.* (2022) primarily concentrated on the synthesis and performance evaluation of CO_2-based PU wood coatings. This involved significant adjustments and modifications to enhance various functional properties, including heat resistance, acid and alkali resistance, hydrophobicity, and flame retardancy, aiming to develop more multifunctional characteristics.

In Malaysia, bamboo wastes generated by the local manufacturing activities could serve as a good source for bio-PU coating. The authors' previous study successfully synthesized bio-PU films from liquefied bamboo (James *et al.* 2024). However, the PU films produced were black in color, which can be less appealing when being used as wood coating. Therefore, bleaching treatment using hydrogen peroxide was applied on the liquefied bamboo prior to PU synthesis. Hydrogen peroxide has been demonstrated to be an excellent bleaching agent that is capable of eliminating the discolouration of heat-treated wood (Akkuş and Budakçı 2020). Such treatment could minimize the physical change such as hardness, gloss, and color of the weathered wood (Budakçı and Karamanoğlu 2014). The results revealed that the bleaching treatment was feasible, and that the treatment only slightly influenced the mechanical and thermal properties of the PU films. In addition, the lighter color of the bleached PU films could be a promising for wood coatings. Therefore, it is important to evaluate the finishing properties of the bio-PU coating. This study evaluated the finishing properties of bleached and unbleached bio-based PU coatings derived from liquefied bamboo. The coatings were applied to rubberwood substrates, and their adhesion, impact resistance, abrasion resistance, and household chemical resistance were assessed.

EXPERIMENTAL

Materials Preparation

Bleached (BLB) and unbleached liquefied bamboo (ULB) from the authors' previous study (James *et al.* 2024) were used for the preparation of bio-PU coating in this study. Polymeric methylene diphenyl diisocyanate (pMDI) and acetone were provided by Sigma Aldrich. The ethyl acetate (EA) was reagent grade and used exactly as received.

Preparation of Bio-PU Coating

The unbleached and bleached liquefied bamboo were diluted with twice the amount of distilled acetone. The solution was then subjected to ultrasonic treatment for 60 s before being vigorously mixed with predetermined pMDI and 10% of EA for an additional 20 s.

The bio-PU was prepared at an NCO/OH ratio of 2.2 based on the optimization study conducted in the authors' previous study (James *et al.* 2024).

Preparation of Rubberwood Substrate

Rubberwood (*Hevea brasiliensis*) sawn timbers were obtained from a Malaysian sawmill in Selangor. The rubberwood samples were cut into size of 1200 mm x 140 mm x 20 mm. Prior to finishing, the lumber was air dried and kept at 25 ± 2 °C for at least 24 h until the MC reached 12 ± 3%. To ensure the surface of the sample was smooth for finishing application, the rubberwood was sanded with 100-grit sandpaper, then 180-grit, and finally with 360-grit sandpaper.

Finishing Application

The bio-PU coating prepared from unbleached and bleached liquefied bamboo was applied to the rubberwood. The amount of bio-coating used was calculated based on the information provided in the previous study (James *et al.* 2024). Four layers of coating were applied to the samples. Sanding was performed between each layer prior to the application of the next coating. The finishing process was conducted in a laboratory at ambient temperature. In this study, a total of 50 samples were coated. The coated rubberwood samples were cured in an oven at 80 °C for 30 min. The coated wood samples were conditioned for a period of 7 days at a temperature of 23 ± 2 °C and a relative humidity of 65 ± 5% prior to evaluation.

Finishing Properties Characterization

The adhesion test was carried out using the cross-cut tape method, which is based on BS EN ISO 2409 (2013). The coatings were cut at approximately a 45° angle to the grain direction using a 2 mm normalised cutting tool. The two series or parallel cuts were crossed at a 90° angle to achieve a pattern of squares. The samples were brushed, and adhesive tape was placed over the cut area. It was then removed after 5 min and carefully examined using a lighter magnifier (2.5x). The rating was based on the step classification given by the standard.

The scratch resistance was evaluated according to the standard BS EN ISO 1518-1 (2011). The finished rubberwood was clamped onto a panel holder, and then it was weighed on the stylus. The scratching needle, which had a hard hemispherical tip measuring 1 mm in diameter, was used to draw across the surface of the coated test specimen. The needle was drawn perpendicular to the grain direction and at a constant speed of 30 to 40 mm/s. Scratching was performed on different part of the test panels, using an increasing load beginning with load of 1000 g and additional 100 g every step on the scratch needle, until the coating cracked, or the scratch was wider than 0.5 mm. The force level in N, which produced such damage, was defined as a critical scratch, exhibiting to scratching.

The abrasion test was conducted according to ASTM D4060-14 (2014). The surface of the coated panels (W_i) was abraded by rotating the panel under a weighted (300 g) abrasive wheel. The abrasion test was stopped when the substrate surface appeared (W_o), and the result was calculated as a loss in weight. The result of abrasion was reported in milligrams. The weight loss of the samples was calculated.

The impact resistance of finishes was assessed according to the guidelines outlined in BS 3962: Part 6 (1980). A steel ball with a diameter of 19 mm and a weight of 28 g was dropped from a height of 1.8 m for free fall onto the surface of the coating. The quality of

the coating can be determined by evaluating the presence of cracks or any defects on the surface area of the specimen, according to the standard.

The chemical resistance of the coated samples was determined using 8 types of liquids, namely distilled water (cold), distilled water (hot, ~90 °C), 3% acetic acid, ethyl alcohol (50% volume), oil and fats (cooking oil), fruit (orange), condiments (chili sauce), and beverage (hot tea) according to standard ASTM D1308-02 (2013). All liquids were dropped using a disposable pipette (3 drop) per spot. The effect was examined after 24 h on the spot after it is cleaned under laboratory light environment according to an assessment *a* to *h* (*a*-discolouration, *b*-change in gloss, *c*-blistering, *d*-softening, *e*-swelling, *f*-loss of adhesion, *g*-special phenomena, and *h*-no change at all).

Five replicates were tested for every condition. The mean values and standard deviations were calculated, and the mean values were further separated using Least Significant Difference (LSD) test at $p \leq 0.05$.

RESULTS AND DISCUSSION

Analysis of Variance (ANOVA)

Table 1 displays the ANOVA for the effect of bleaching treatment on the finishing properties of the bio-PU coating. The ANOVA showed that unbleached and bleached bio-PU had significant effects on scratch ($p \leq 0.04$) and impact resistance ($p \leq 0.002$), respectively. However, the bleaching treatment had no significant effect on either the adhesion ($p \leq 0.14$) or abrasion properties ($p \leq 0.58$).

Table 1. Summary ANOVA for the Effect of Bleaching Treatment on the Finishing Properties of Bio-PU Coating

Properties	p-value	Significance level
Adhesion	0.1411	ns
Scratch resistance	0.0400	*
Abrasion resistance	0.5818	ns
Impact resistance	0.0023	**

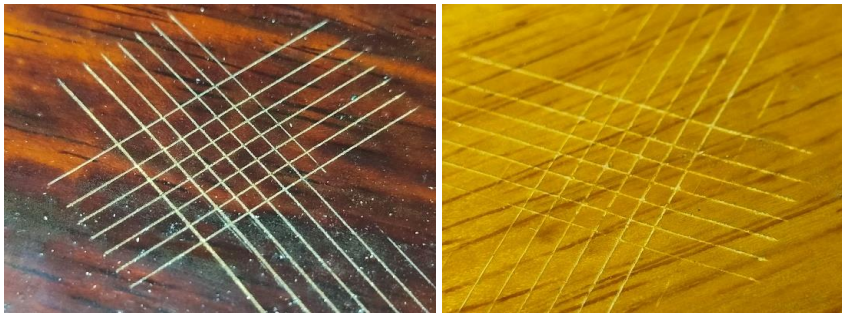
Note: [ns]Not significant at $p > 0.05$; *Significant different at $p \leq 0.05$; **Significant different at $p \leq 0.01$

Adhesion Test (cross-cut)

Figure 1 shows the adhesion resistance of the samples coated with bleached and unbleached bio-PU coating. It can be observed that the color of the coating became significantly lighter after bleaching treatment. However, the bleaching treatment did not affect the adhesion properties of the bio-PU coating, as both bleached and unbleached bio-PU coating had an adhesion rating of 1, where a cross-cut area not greater than 5% is affected. Adhesion rating of 1 represents good adhesion properties and is generally well accepted for commercial organic coatings (Cheumani *et al.* 2021).

The authors' previous study reported that the bleaching treatment has some minor negative impact on the mechanical and thermal stability of the PU film (James *et al.* 2024). However, it can be overcome by increasing the NCO/OH ratio. In this study, NCO/OH ratio of 2.2 were used for the preparation of bio-PU coating as compensatory measure. It is well known that adhesion depends on chemical interaction and mechanical interlocking at the interface (Kong *et al.* 2013). Adhesion is favourably affected by the more polar

urethane and ester groups, which involves sufficient adhesion and toughness to the coating (Patel *et al.* 2014). A high NCO/OH ratio generally increases the cross-linking density of the PU polymers and consequently the mechanical properties (strength, hardness) of the final products. Therefore, this might be the reason the adhesion properties did not differ significantly between bleached and unbleached bio-PU coating.



a **b**

Fig. 1. Adhesion resistance of UPU (a) and BPU (b) coated samples

Scratch Resistance

Figure 2 shows the scratch resistance of bleached and unbleached bio-PU coating. Bleaching treatment prior to PU synthesis appeared to reduce the scratch resistance of the coating significantly. Unbleached bio-PU (UPU) showed significantly higher scratch resistance of 19.7 N than bleached bio-PU (BPU) at 19.04 N. The lower scratch resistance in BPU is possibly due to the presence of salts from sodium hydroxide. These salts may impact the quality of cured polyurethane films based on liquid polyol.

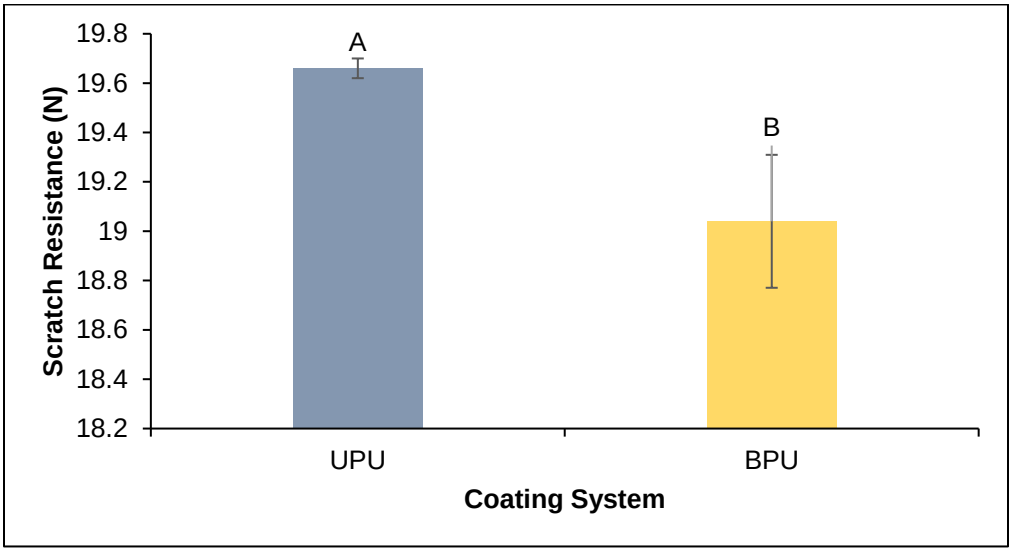


Fig. 2. Scratch resistance of UPU and BPU coated wood
Note: Bar charts followed by the same letters [A, B] were not significantly different at $p \leq 0.05$ according to LSD

The scratch marks of both the BPU and UPU coating are displayed in Fig. 3. Despite having significantly lower scratch resistance compared to UPU, BPU still showed higher scratch resisting capability. In fact, because of its lighter color, the scratch marks on

the BPU samples were less obvious compared to those of UPU. The scratch resistance of cellulose nitrate lacquer, polyurethane, and various wood varnishes was reported to be between 1.5 N and 6 N in previous studies (Çakıcıer *et al.* 2011; Cheumani Yona *et al.* 2021), which is much lower compared to UPU and BPU coating in this study.

a **b**

Fig. 3. Scratch marked of UPU (a) and BPU (b) coated samples

Abrasion Resistance

As shown in Table 2, the weight loss of UPU and BPU coated wood after the abrasion test for 500 cycles was 0.024 g and 0.070 g, respectively. Meanwhile, the recorded abrasion at 1000 cycles was 0.053 g and 0.12 g, respectively. After 500 cycles, BPU coating lost almost 2-folds (192%) weight compared to UPU coating. Meanwhile, the weight loss of BPU coating was 126% higher than UPU coating at 1000 cycles. However, the abrasion resistance of these UPU and BPU coating fall within the required range for polyurethane floor coatings (< 150 mg), suggesting that these materials are suitable for hard floor coatings (Kong *et al.* 2013).

Table 2. Abrasion Resistance of UPU and BPU Coatings

Type of Coating	Weight Loss After 500 Cycles (g)	Difference (%)*	Weight Loss After 1000 Cycles (g)	Difference (%)
UPU	0.024	-	0.053	-
BPU	0.070	191.7	0.12	126.4

*Note: Difference in mass loss between UPU and BPU under the same cycles

a b

Fig. 4. UPU (a) and BPU (b) coated wood after abrasion test for 1000 cycles

The appearance of the wood samples after abrasion test is shown in Fig. 4. After subjecting UPU and BPU coated wood to an abrasion test for 1000 cycles, abrasion rings were observed on the surface. The surface of the BPU coated wood is clearly visible while it is less visible in the UPU coated wood. This observation suggests that the UPU has better abrasion resistance than BPU coating.

Impact Resistance

Figure 5 shows the impact resistance of UPU and BPU coating. As shown in Fig. 5, no surface cracking was observed on the UPU coating, giving a rating of 5, which indicates superior impact resistance of UPU coating. Meanwhile, some slight cracking around the edge of the indentation was observed in BPU-coated sample, giving a rating of 4. The impact resistance appeared to be lowered by the bleaching treatment prior to PU synthesis. Similar to scratch resistance, the impact resistance rating revealed that the surface hardness of UPU coating was higher than that of BPU coating.

a b

Fig. 5. Impact resistance of UPU (a) and BPU (b) coated wood

Household Chemical Resistance

Table 3 shows the performance of the UPU and BPU coated samples after 24 h exposure to household chemicals. These results indicated that bio-coating demonstrated good resistance to all selected household chemicals within the exposure time, except for acetic acid. Blistering was observed after exposure to acetic acid (Fig. 6).

Table 3. Assessment of the Effects of Household Chemicals on UPU And BPU-Coated Surfaces

Coating System / Household Chemical		UPU	BPU
1	Distilled water (cold)	*h*	*h*
2	Distilled water (hot)	*h*	*h*
3	Acetic acid 3%	*c*	*c*
4	Ethyl alcohol 50% volume	*h*	*h*
5	Oil and fats (cooking oil)	*h*	*h*
6	Fruit (orange)	*h*	*h*
7	Condiment (chilli sauce)	*h*	*h*
8	Beverage (hot tea)	*h*	*h*

Note: *c*, blistering; *h*, no change at all

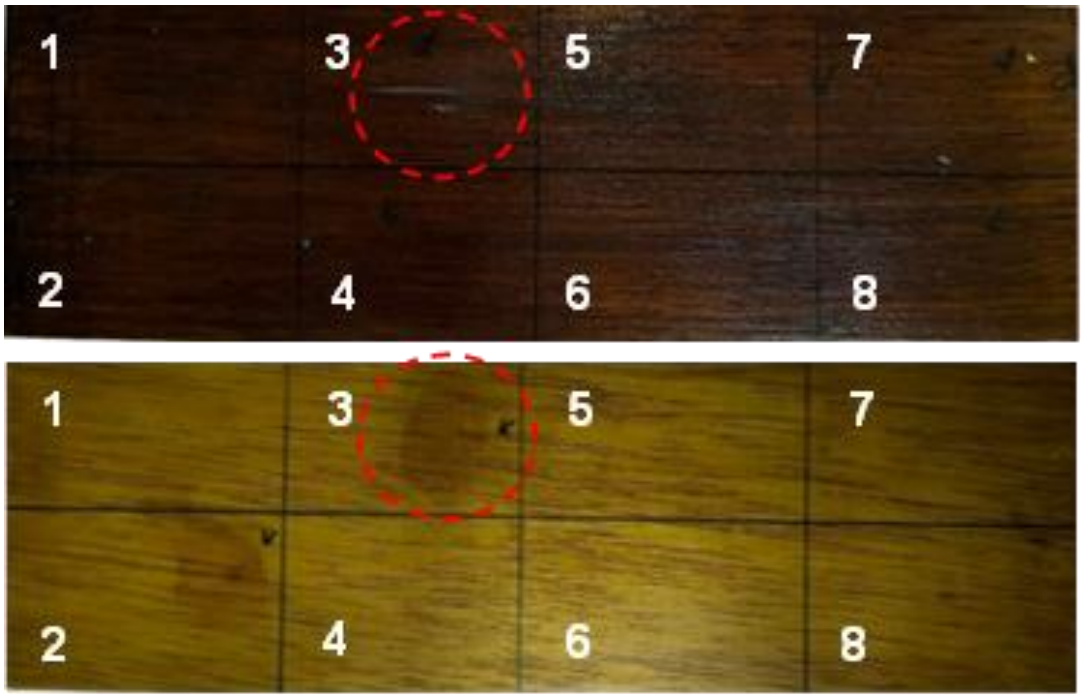


Fig. 6. Household chemical effects on UPU (upper) and BPU (lower) after exposure for 24 h

This discovery aligns with Raychura *et al.*'s (2018) findings that indicated polyurethane coatings exhibited excellent performance in beverage stain tests, were easy to clean, and showed no residual spots after wiping. Meanwhile, acid solution (pH 3) had a negative effect on the coating properties. This finding could be due to hydrolysis of the urethane or ester bonds in the presence of acid (Jin *et al.* 2022), which results in a deterioration of strength. The findings indicated that the bleaching treatment did not have a significant effect on the household chemical resistance of the PU coating.

CONCLUSIONS

1. The bleaching treatment before polyurethane (PU) synthesis had a mixed effect on the properties of the surface finish.

2. Adhesion and abrasion resistance of both bleached and unbleached bio-PU coating did not differ significantly although bleached bio-PU coating displayed slightly lower abrasion resistance.
3. Bleached bio-PU coating had significantly lower scratch resistance and impact resistance compared to unbleached bio-PU coating. However, the scratch resistance of bleached bio-PU coating was still higher compared to various wood varnishes.
4. Both bleached and unbleached bio-PU coating had good resistance against various household chemicals, with exception of acetic acid. The findings in this study revealed that the bleached bio-PU coating is suitable for flooring applications. Bleaching treatment resulted in some impacts on the finishing properties of the PU coating, but the impact could be minimized by using higher NCO/OH ratio.

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