Review paper: properties of low molecular weight phenol formaldehyde – treated bamboo composite

Trinh Hien Mai[1], Nguyen Thị Tham[1], Nguyen Tat Thang[1], Nguyen Thi Yen[1], Nguyen Van Huyen[1], Tang Thi Kim Hong[2]

[1]*Vietnam National University of Forestry*

[2]*Nong Lam University, Ho Chi Minh City*

Tính chất của vật liệu compozit tre xử lý với nhựa phenol formaldehyde phân tử lượng thấp

Trịnh Hiền Mai[1], Nguyễn Thị Thắm[1], Nguyễn Tất Thắng[1], Nguyễn Thị Yến[1], Nguyễn Văn Huyến[1], Tăng Thị Kim Hồng[2]

[1]*Trường Đại học Lâm nghiệp*

[2]*Trường Đại học Nông Lâm TP.HCM*

https://doi.org/10.55250/jo.vnuf.8.2.2023.159-164

Article info:
Received: 24/05/2023
Revised: 28/07/2023
Accepted: 25/09/2023

Keywords:
bamboo, bonding quality, low molecular weight PF resin, mechanical properties, physical properties.

ABSTRACT

Impregnation of bamboo in phenol formaldehyde (PF) solution is one of the promising solutions to overcome the drawback of the material. The use of low molecular weight PF resin (LMW PF) in the production of bamboo composite materials not only improves the dimensional stability but also increases the mechanical strength of the material. The bonding interface between bamboo elements and adhesives is presumed to be significantly influenced by the degree of adhesive penetration into the porous network of interconnected cells of bamboo surfaces. The permeation of PF resins in bamboo is closely related to their molecular weight. LMW PF resin will overpenetrate and lead to an undesirable starved bondline while high-MW PF resins only remain in the bondline and it is difficult to form mechanical interlocking. This paper discusses the research results on the bonding quality of bamboo strips when impregnated in LMW PF solution with different ratios and different pressing technology parameters; at the same time, physical and mechanical properties of bamboo composite materials treated with PF PTLT such as: water absorption resistance, dimensional stability, bonding strength, modulus of rupture (MOR), modulus of elasticity (MOE) are also significantly improved. This is a scientific basis that can serve as a premise for the research on technology to produce composite materials from bamboo and LMW PF in Vietnam.

Từ khóa:
chất lượng dán dính, nhựa PF phân tử lượng thấp, tính chất cơ học, tính chất vật lý, tre.

TÓM TẮT

Ngâm tẩm tre trong dung dịch PF là một trong những giải pháp hứa hẹn để khắc phục các nhược điểm của vật liệu. Việc sử dụng nhựa PF phân tử lượng thấp (PF PTLT) trong sản xuất vật liệu composite tre không chỉ cải thiện độ ổn định kích thước mà còn giúp gia tăng độ bền cơ học của vật liệu. Bề mặt liên kết giữa các phần tử tre và chất kết dính chịu ảnh hưởng đáng kể của mức độ thấm sâu của chất kết dính vào trong khoảng trống giữa các tế bào ở lớp bề mặt của tre. Bài báo này thảo luận về các kết quả nghiên cứu về chất lượng dán dính của các thanh tre khi ngâm tẩm trong dung dịch PF PTLT với các tỷ lệ khác nhau và thông số công nghệ ép khác nhau; đồng thời, tính chất vật lý và cơ học của vật liệu composite tre sử dụng PF PTLT như: khả năng chống hút nước, độ ổn định kích thước, độ bền dán dính, độ bền uốn tĩnh, modul đàn hồi uốn tĩnh... cũng được cải thiện đáng kể.

1. INTRODUCTION

Bamboo is a known biomass material for its high renewability, fast-growing, sustainability, and energy efficiency. It exhibits the highest specific strength compared to traditional timber, concrete, structural steel and so on. Bamboo has been employed in fabricating engineered bamboo composites, including bamboo scrimber, laminated bamboo lumber, and bamboo plywood, in response to the growing need for sustainable construction materials [1, 2]. However, bamboo and other lignocellulosic materials are unstable when subjected to high moisture environment. Impregnation of wood/bamboo with phenolic resin is one of several promising methods to overcome the weakness of composite products, in particular its dimensional instability. Phenol-formaldehyde resin, renowned as one of the most moisture-durable wood adhesives, is frequently employed within the engineered bamboo industry [2, 3]. Apart from factors such as surface energy, wetting characteristics, surface roughness, and the formation of a weak boundary layer [4], the diffusion of adhesive compounds into the bamboo cell wall is a factor that may affect adhesive bonding performance. Numerous investigations have explored the adhesive penetration and mechanical properties of the interface between wood and adhesives using variety of analytical techniques [5, 6]. Nonetheless, there is a scarcity of research on resin penetration into bamboo surfaces and its influence on the bonding interface between bamboo and resin [7, 8], though adhesion and properties of LMW PF - treated plybamboo samples have been studied [9, 10]. The aim of this study is to discuss the adhesion, bonding properties and physical, mechanical propeties of LMW PF - treated bamboo composite material.

2. ADHESION AND BONDING PROPERTIES OF BAMBOO COMPOSITES TREATED WITH LOW MOLECULAR WEIGHT PHENOL FORMALDEHYDE

Water-soluble phenol-formaldehyde resin is commonly used in the bamboo-based panels industry [9-12]. However, there remains uncertainty about whether the formation of an interpenetrating network by PF resin penetration on the bamboo surface can be achieved compared to wood. This uncertainty arises from the intrinsic absence of horizontal organization in bamboo, such as wood rays and so on. Furthermore, bondline thickness and bondline strength resulting from adhesive penetration play a significant role in determining the shear strength of a composite material [13, 14]. All of these unusual and noteworthy factors impact the extensive utilization of PF in engineering materials derived from bamboo.

The permeation of PF resins in wood/bamboo is closely related to their molecular weight. LMW PF resin can penetrate excessively, resulting in an undesired starved bondline, whereas high-MW PF resins tend to stay within the bondline, making the formation of mechanical interlocking challenging. Hence, to establish an effective bonding interface, it is necessary for some LMW PF resins to penetrate into cells to form glue nails; at the same time, some high-MWPF resins should remain within the bondline to ensure both their thickness and strength [2]. In the study of Huang *et al*. 2020, bromine-labelled PF (BrPF) resins with four varying molecular weights were employed to create bamboo/adhesive interfaces, aiming to assess the distribution of PF resin. The four BrPFs were utilized to glue two-plybamboo panels together. The test specimens were proccesed with a press-cured at 150°C for 25 min under a pressure of 0.6 MPa and the amount of glue spread was 100 g m^{-2}. Ultra-depth-of-field microscopy and SEM-EDS were applied to visualize the penetration of BrPF resin into bamboo cells and bamboo cell walls at various scales. IR and NMR were utilized to identify molecular-level interactions between PF resin and bamboo cell walls. The study encompassed the examination of four distinct BrPF resins with varying molecular weights. The findings indicated that LMW PF resins exhibited the deepest penetration into bamboo, effectively infiltrating the bamboo cell wall, and reinforcing the cell wall matrix. Conversely, high-MW resins predominantly remained within the bondline. Besides mechanical interlocking, the study unveiled the formation of covalent bonds and hydrogen bonds resulting from reactions between bamboo components and PF resins during the curing process. With above results, the dual adhesive dispensing method, incorporating both LMW and high-MW resins, was employed to enhance the bonding quality of two-plybamboo panels.

The bonding interface between bamboo components and adhesives is believed to be substantially influenced by the extent of adhesive infiltration into the porous network of interconnected cells on the surface of bamboo. The study of Guan *et al.* (2014) [15] was performed with convention PF resin and LMW PF resin with an average molecular weight of 2036 and 810 respectively. Then, these two resins were mixed together according to different ratios (10:0.5, 10:1 and 10:2). Two-ply Moso bamboo (*Phyllostachys pubescens*, 4 years old) was glued together by above modified adhesives, panels parallel to each other (each ply is 5 mm). The specimens were all press-cured for 15 min at pressure of 2 MPa and at temperature of 140°C. Research results showed that, LMW PF has the ability to migrate and accumulate into the cell wall on the bamboo surface when heat pressed and thus stabilize the cell wall and reduce the interfacial stress concentration. However, the degree of cross-linking and polymer chain of LMW PF is not as good as that of conventional PF glue because the chaos in the bonding interface regions increases as the percentage of LMW PF increases. In this study, the 5% LMW PF sample was not enough to fill (internal void) the cell wall, while the 20% LMW PF sample was too excessive to fill the internal void of the cell wall, thus leading to decreased thickness of the adhesive film and weakening of the mechanical interlock bond of the interfacial bondline. Moreover, the introduction of LMW PF into the bondline resulted in a disordered strain distribution around the bondline regions, potentially disrupting strain transmission and leading to slippage of the bamboo bonding interface. As a result, the 10% LMW PF sample exhibited the best performance. This can be attributed to its smaller strain values on the bonding surface and improved distribution of the chaotic region compared to the other samples. When the percentage of LMW PF increased, the shear strength of the adhesive film in the dry state reached a maximum value of 14.08 MPa at 10% LMW PF content, while this value was at least 8, 03 MPa when the LMW PF content is 20%. Modified PF adhesive with 10% LMW PF not only meets the requirement of mechanical bonding of bamboo bonding surface depth, but also stabilizes the cell wall to create a bridge and alter its mechanical properties. However, the tensile strength of the adhesive film in the wet state in particular decreased significantly when increasing the proportion of PF LMW in the modified PF adhesive (from 10 MPa to 7.11 MPa).

Anwar *et al.* (2012) [10] examined the adhesion of bamboo (*Gigantochloa scortechinii*) strips following impregnation with phenolic resin and explored the effect of curing duration on the bonding characteristics of LMW PF-treated plybamboo. The four-year-old bamboo culms were cut into segments of 20 mm wide and planed to 4–5 mm thick to produce bamboo strips and dried to a moisture content of 10%. The LMW PF resin, with an average molecular weight of 600, was used to ensure that the resin could easily penetrate into bamboo strips during impregnation process. Bamboo strips were impregnated with LMW PF resin in a vacuum pressure impregnation processing tank and evacuated at 750 mm Hg for 1 hour. Subsequently, the bamboo strips were dried in an oven at a temperature of 60°C for 9 hours, resulting in an average weight percentage gain of 14% for the LMW PF-treated strips. In producing plybamboo, the treated or untreated bamboo strips were bonded together edge-to-edge using phenol-resorcinol-formaldehyde resin to create bamboo veneer. Bamboo veneers were subsequently arranged at right angles to each other, creating three-layer (12 mm in thickness) and five-layer plybamboo (20 mm in thickness) with PF resin serving as the binding agent. The plybamboo was then subjected to hot pressing at 140°C and a 14 $kg.m^{-2}$ pressure. Pressing times of 11, 22, 33 and 44 min were applied to plybamboo treated with LMW PF. The study results indicated that bamboo strips treated with phenolic resin exhibited greater contact angles and were less permeable to liquids than untreated strips. The buffering capacity analysis showed that bamboo strips exhibited stability towards acid. Tensile strength of the plybamboo met the requirement of BS EN 314-1. The study concluded that the optimum pressing times were 22 and 33 min for three- and five-layer plybamboo respectively to produce good bonding quality. The results of this study demonstrated that the treatment of bamboo strips with LMW PF resin led to a significant decrease in the wettability of the treated strips, following a trend similar to that observed in wood. As a result, the adhesive formulation for bonding phenolic-treated bamboo strips may resemble that used for wood, where the incorporation of fillers or extenders to control adhesive penetration may not be required.

3. PHYSICAL AND MECHANICAL PROPERTIES OF LOW MOLECULAR WEIGHT PHENOL FORMALDEHYDE - TREATED BAMBOO COMPOSITE

Rao *et al.* (2020) [16] evaluated the water resistance and mechanical strength of bamboo composite made from 4-year-old Moso bamboo (*Phyllostachys pubescens* Mazel) and LMW PF resin with solid content of 47.91%, viscosity of 35 cps, and pH of 10–11. Bamboo was cut horizontally to a length of 2.6 m, splitted and dried to a moisture content of about 7%. The PF resin was added purified water and diluted into 20 wt% and 30 wt% solutions. Next, the dried oriented bamboo fiber mats (OBFMs) were immersed in the resin solution at room temperature for approximately 6 minutes. To attain the targeted PF resin concentrations (10, 15, 20, and 25 wt%), the mats were removed, drained for 4 to 8 minutes to eliminate excess resin, and weighed. Then, the OBFMs were left to air dry until they reached a moisture content of approximately 12 wt%. After being weighed, all the mats were arranged symmetrically with their grain orientation, placing the outer layer outward and the inner surface inward such that they could be uniformly and loosely laid, forming slabs within a mold measuring 300 x 170 x 15 mm (length x radial x tangential) for hot-pressing using a hot press machine. During this process, the slabs were pressed at a temperature of 150°C, with a holding time of 0.5 min/mm. The pressure was maintained within the 3.5–7.0 MPa range to cure the mats. Finally, outdoor bamboo-fiber-reinforced composite (OBFRC) slabs with target resin contents of 10, 15, 20 and 25 wt% were obtained. The technology diagram for the production of bamboo composites (OBFRC) is shown in Figure 1.

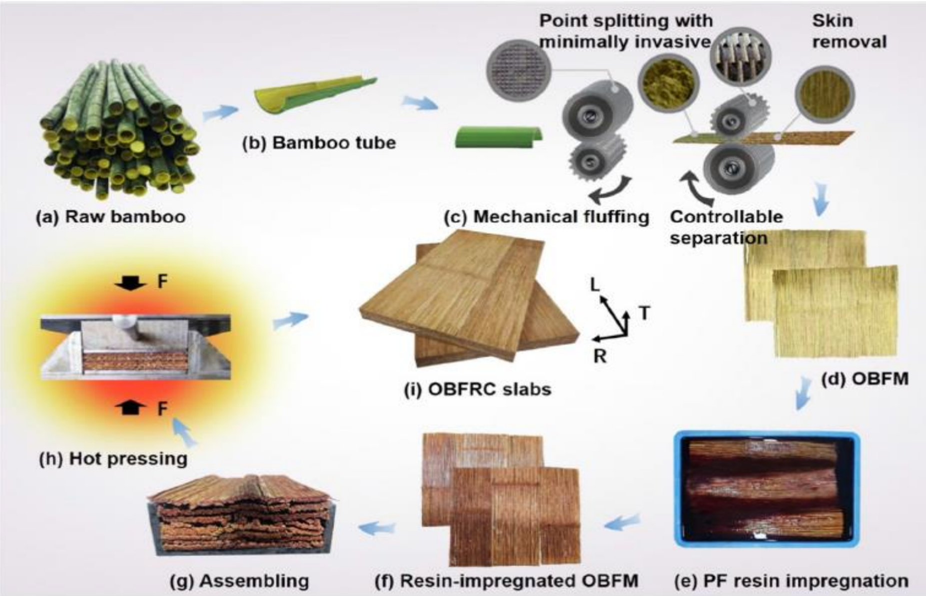

Figure 1. Production of bamboo composites (OBFRC) [16]

The results revealed that water resistance gradually improved as the resin content in OBFRC products increased. Shear strength initially increased, then gradually declined, while compressive strength steadily decreased. There was no significant change in water resistance due to increasing the resin content from 20% to 25%. However, the mechanical properties notably declined, suggesting that the optimal resin content for OBFRC is 20%. It's worth noting that the mechanical properties of OBFRC formulated with resin contents ranging from 10% to 25% surpass those of bamboo composites and substantially exceed the highest levels specified in GB/T 20241-2006 and GB/T 30364-2013. This indicated that OBFRC holds substantial potential for applications in structural and engineering fields. Likewise, in comparison to new wood-based products, OBFRC produced with a resin content of 20% demonstrates exceptional water resistance, falling well below the requirements for high-grade outdoor-use bamboo scrimber products outlined in GB/T 30364-2013. Given its impressive strength, modulus, and water resistance, this OBFRC holds significant promise as a viable alternative to existing engineered bamboo and wood products for applications in outdoor flooring and building construction.

In the study conducted by Yanglun Yu *et al.* (2018) [17], Ci bamboo (*Neosinocalamus affinis*) aged three years and featuring a diameter of 50-60 mm, bamboo wall thickness of 4–5 mm was impregnation with PF resin (trade name PF16L510), a LMW resin, with a solid content of 46%, a viscosity of 40.5 CP_s, and a pH value of 10-11. The bamboo was initially cut into bamboo tubes measuring 2,600 mm in length. Afterward, these bamboo tubes were split longitudinally into two semicircular bamboo tubes. The bamboo tubes were then fluffed along the longitudinal fiber direction to create a pattern of dotted and/or linear-shaped cracks running along the fiber direction. As a result, structured and oriented bamboo fiber mats (OBFMs) were successfully produced. They were then placed in an oven and dried to an approximate moisture content of 10%. Afterward, the OBFMs were submerged in the PF resin for 6 minutes at room temperature. Then, the mats were removed and leaked for about 6–10 minutes to remove excess resin and were weighed to ensure that the resin loading reached 13% w/w. After that, the bamboo fiber bundles were dried in an oven at 60°C to reach a moisture content of 12% w/w. The composites were manufactured using compression molding technology. Bamboo fiber bundles were assembled along the grain direction in the hot-pressing mold at 160°C and a pressure of 6.0 MPa, with a 1 min/mm holding time. The target density of the composites was 1.02 g/cm^3 and 1.30 g/cm^3, respectively, at size of 2.6 m (length) x 1.3 m (width) x 0.16 m (thickness). The modulus and strength of the resulting composite with a density of 1.30 g/cm^3 were 32.3 GPa and 398 MPa, respectively, whereas those of the raw bamboo were 13.5 GPa and 178 MPa, respectively. The composite boasted nearly twice the fiber content per unit volume compared to bamboo, indicating substantial densification of the bamboo. Moreover, the thin-walled cells of bamboo fiber-reinforced composites exhibited a remarkable increase of 41.77% and 47.95% in MOE and hardness, respectively, signifying a significant enhancement in the performance of ground tissues. Whereas those of the fiber cells only increased by 7.16 and 3.75%, espectively. The intercellular space and cell cavity were filled with resins and mechanical bonding was formed between the fiber cells and ground tissues, indicating the enhancement of the intercellular layer.

Anwar *et al.* (2009) [9] conducted a study investigating the effect of pressing time on phenolic-impregnated bamboo strips' physical and mechanical properties. They focused on bamboo strips (*Gigantochloa scortechinii*) impregnated with LMW PF resin. Samples were immersed in LMW PF resin using a 750 mmHg vacuum chamber for 1h before releasing for 1.5 h. The treated strips were dried in an oven at 60ºC for 6 to 9 h. They were hot pressed at 14 kgm^{-2} at 140ºC for 5, 8, 11, 14 and 17 min. Upon analyzing the physical and mechanical properties of the strips, it was evident that the phenolic-treated strips exhibited a substantial improvement compared to the control samples. The dimensional stability, including water absorption, thickness swelling, and linear expansion, exhibited notably lower values in the phenolic-treated strips than in the control samples after a 5-min pressing time. The phenolic-treated strips' anti-shrink efficiency (ASE) increased as the pressing time was extended from 5 to 17 min. The average modulus of rupture (MOR) for the control samples, which measured 177 Nmm^{-2}, exhibited a noteworthy contrast with the phenolic-treated strips after a 17-minute pressing time (224

Nmm^{-2}). However, the study revealed no substantial difference in compression parallel to the grain. The MOE for the phenolic-treated strips was 21,777 Nmm^{-2}, while for the control was 18,249 Nmm^{-2}. Similarly, the compression parallel to the grain values for the phenolic-treated and control samples were 94 and 77 Nmm^{-2}, respectively.

4. CONCLUSIONS

There have been many studies on the production technology of composite materials from bamboo and LMW PF. The results show that the LWM PF resin can penetrate and accumulate into the interconnected cells. The penetration of PF resins in bamboo is closely related to their molecular weight. LMW PF resin can infiltrate excessively, resulting in an undesirably starved bondline, whereas high-MW PF resins remain primarily within the bondline, making it challenging to establish effective mechanical interlocking. Additionally, treatment with LMW PF resin substantially enhances most of the physical and mechanical properties of bamboo composite materials. Therefore, this is a scientific basis that can serve as a premise for the research on technology to produce composite materials from bamboo and LMW PF in Vietnam.

REFERENCES

[1]. Xiaoqing Wang & Haiqing Ren (2008). Comparative study of the photo-discoloration of moso bamboo (Phyllostachys pubescens Mazel) and two wood species. Applied surface science. 254(21): 7029-7034.

[2]. Yuxiang Huang, Qiuqin Lin, Chan Yang, Guomin Bian, Yahui Zhang & Wenji Yu (2020). Multi-scale characterization of bamboo bonding interfaces with phenol-formaldehyde resin of different molecular weight to study the bonding mechanism. Journal of the Royal Society Interface. 17(162): 20190755.

[3]. MT Paridah, LL Ong, A Zaidon, S Rahim & UMK Anwar (2006). Improving the dimensional stability of multi-layered strand board through resin impregnation. Journal of Tropical Forest Science. 166-172.

[4]. Frederick A Kamke & Jong N Lee (2007). Adhesive penetration in wood—a review. Wood and Fiber Science. 205-220.

[5]. G Modzel, FA Kamke & F De Carlo (2011). Comparative analysis of a wood: adhesive bondline. Wood Science and Technology. 45: 147-158.

[6]. Andreas Valla, Johannes Konnerth, Daniel Keunecke, Peter Niemz, Ulrich Müller & Wolfgang Gindl (2011). Comparison of two optical methods for contactless, full field and highly sensitive in-plane deformation measurements using the example of plywood. Wood science and technology. 45: 755-765.

[7]. MingJie Guan, Cheng Yong & Jia Zhao (2012). Characterization on bamboo bonding interface by fluorescent track. Journal of Nanjing Forestry University (Natural Sciences Edition). 36(5): 125-128.

[8]. Mingjie Guan, Cheng Yong & Lu Wang (2013). Shear strain and microscopic characterization of a bamboo bonding interface with poly (vinyl alcohol) modified phenol–formaldehyde resin. Journal of Applied Polymer Science. 130(2): 1345-1350.

[9]. UMK Anwar, MT Paridah, H Hamdan, S Mohd Sapuan & ES Bakar (2009). Effect of curing time on physical and mechanical properties of phenolic-treated bamboo strips. industrial crops and products. 29(1): 214-219.

[10]. UMK Anwar, MT Paridah, H Hamdan, A Zaidon, A Roziela Hanim & AS Nordahlia (2012). Adhesion and bonding properties of low molecular weight phenol formaldehyde-treated plybamboo. Journal of Tropical Forest Science. 379-386.

[11]. Ming-jie Guan, Yi-xin Zhu, Xiao-dong Zhang & Qi-sheng Zhang (2005). Bending properties of wood-bamboo composite plywood in differently hygrothermal conditions. Journal Of Nanjing Forestry University. 48(06): 106.

[12]. Mingjie Guan, Yixin Zhu & Xin'an Zhang (2006). Comparison of bending properties of scrimber and bamboo scrimber. Dongbei Linye Daxue Xuebao (Journal of Northeast Forestry University). 34(4): 7.

[13]. Erik Serrano & Per Johan Gustafsson (1999). Influence of bondline brittleness and defects on the strength of timber finger-joints. International Journal of Adhesion and Adhesives. 19(1): 9-17.

[14]. John Tomblin, Pierre Harter, Waruna Seneviratne & Charles Yang (2002). Characterization of bondline thickness effects in adhesive joints. Composites Technology and Research. 24(2): 332-344.

[15]. Mingjie Guan, Cheng Yong & Lu Wang (2014). Microscopic characterization of modified phenol-formaldehyde resin penetration of bamboo surfaces and its effect on some properties of two-ply bamboo bonding interface. BioResources. 9(2): 1953-1963.

[16]. Fei Rao, Yaohui Ji, Neng Li, Yahui Zhang, Yuhe Chen & Wenji Yu (2020). Outdoor bamboo-fiber-reinforced composite: Influence of resin content on water resistance and mechanical properties. Construction and Building Materials. 261: 120022.

[17]. Yanglun Yu, Yuxiang Huang, Yahui Zhang, Ru Liu, Fandan Meng & Wenji Yu (2019). The reinforcing mechanism of mechanical properties of bamboo fiber bundle-reinforced composites. Polymer Composites. 40(4): 1463-1472.