

Article

Preparation of Wood-Based Panel Composites with Poplar Veneer as the Surface Layer Modified by In-Situ Polymerization of Active Monomers

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Abstract: Wood-based panels covered by melamine-impregnated paper are widely used in floors and furniture, due to its good surface texture, hardness, wear resistance, and waterproof function. However, there are still some problems, such as formaldehyde release from the impregnated resin, non-wood touch, and complex preparation processes. Therefore, this study designed glycidyl methacrylate (GMA) and ethyleneglycol dimethacrylate (EGDMA), combined with maleic anhydride (MAN) as a reactive catalyst, to build an active monomers system. It was first impregnated into poplar veneers, and then in-situ polymerized within the veneer using a hot pressing process, which realized the gluing of the veneer onto the wood-based panel substrate, synchronously. Such treatment aims to obtain wood-based panel composites decorated by the modified veneer, with real solid wood touch feeling, satisfied surface properties, and environment friendly glue bonding. The results indicated that the optimized reaction ratio of the active monomers (GMA:EGDMA) was 2:1 (molar ratio), and the maleic anhydride addition accounted for 6 wt.% of the total monomers. Under the optimized hot pressing condition, the modified veneer closely bonded to the wood-based panel substrate without obvious interfacial gaps. The hardness, abrasion resistance, modulus of rupture, and water resistance of the composites were significantly improved. Such results indicate that the treatment realized the perfect merging of solid wood touch feeling, environment friendly feature, and excellent properties of the composite. It was highly expected to replace the traditional melamine-impregnated paper to decorate wood-based panels, and could be potentially applied as surface decorating materials in wide areas of desktop, floor, cupboard, wardrobe, and so on.

Keywords: wood veneer; active monomer; impregnation; in-situ polymerization; veneer decorated wood-based panel composite; hot pressing; glue bonding

1. Introduction

Wood is widely used in construction, home residence, transportation, and other fields because of its advantages, such as light weight, high strength, beautiful texture, cheap and easy availability,



environment friendly feature, and renewability, which are all favorite among people [1–4]. In recent years, with the economic development and improvement of people's life quality, human demand for wood has increased. However, the supply of high-quality wood has become increasingly scarce; and thus the contradiction between wood supply and demand has become increasingly prominent [5,6]. Therefore, people turn to explore low-quality and fast-growing wood species and wood processing residues, for preparing various wood-based panels to meet the urgent needs of people for wood [7–11]. However, the surfaces of the traditional wood-based panels have some common disadvantages, such as non-texture, lower abrasion resistance and hardness, and strong water absorption capacity, which make them difficult to be directly used as wooden panel materials for floor, desktop board, cabinet panel, etc. [12–14]. Therefore, melamine-impregnated paper is usually employed to glue on the panels' surface, to overcome the above drawbacks of the wood-based panels [15,16]. This method makes the panels that are widely used as decorating materials in floor, furniture, wooden doors, cabinets, and bath cabinets, which not only improves the application value of the wood-based panels, but also broadens its application fields [17,18]. Such melamine-impregnated, paper-decorated, wood-based

However, there are still some shortcomings in the technology of paper decorating wood-based panels, such as, the product surface is non-real wood touch, and the melamine glue to impregnate paper releases formaldehyde, and the preparing process of the wood-based panels improves their real wood texture, the following coating treatment decreases their real wood touch, and complicates the preparation processes [22,23]. Therefore, this study proposed the following structural design—non-formaldehyde active monomers are impregnated into the veneer, and glue bonds the veneer and the wood-based panels to form a veneer-decorated panel composite. The active monomers were designed to simultaneously realize the in-situ polymerization and glue bonding, via one hot pressing process. This method aimed to improve the strength, abrasion resistance, hardness, water resistance of the veneer surface, and to also convey real wood touch to the wood-based panels [24–26]. It potentially provides a new way for low-quality wood to realize high-value utilization, and extends the panel types to provide another choice for household materials.

panels are now one of the most popular wood-based materials in the market.

Previous studies reported that acrylic monomers could polymerize in situ to reinforce wood. However, the monomers are normally easy to evaporate, even under ambient conditions, and the resultant polymers within wood are normally thermoplastic, which could cause thermoplastic flow under hot-pressing conditions, and thus, are incapable of adapting to the gluing process [27,28]. Given the structural analysis of the designed active monomers, both glycidyl methacrylate (GMA) and ethyleneglycol dimethacrylate (EGDMA) have C=C bonds, which could theoretically form polymer networks to reinforce veneer via the free radical copolymerization [29,30]. Additionally, GMA has an epoxy group, which could theoretically react with the hydroxyl groups on wood components, via the epoxy ring opening reaction, especially under the catalysis of acid condition, derived from the potential reaction of maleic anhydride (MAN) and the hydroxyl group. Therefore, this study designed GMA and EGDMA as the active monomers, and MAN as the catalyst, to build a reaction system to modify the wood veneer. In terms of the bonding strength of the national standard GB/T 15104-2006 "Decorative Veneer Wood-Based Panel", we mainly studied the optimized preparation craft of the modified veneer-decorated wood-based panel composites, including the reaction ratio of the active monomers, the catalyst content, and the hot pressing conditions (temperature, pressure, and time). Furthermore, the surface abrasion resistance, surface hardness, water resistance, and bending strength of the composites were tested and evaluated. The results show that the modified veneer has the potential to replace the melamine-impregnated paper and decorate the wood-based panel for new composites.

2. Experimental Materials and Methods

2.1. Experimental Materials

GMA (Nanjing Jiulong Chemical Industry Co., Ltd., Nanjing, China), EGDMA (Yantai Yuntai Chemical Industry Co. Ltd., Yantai, China), MAN (Shanghai Chemical Reagent Factory, Shanghai China) and 2,2'-azobisisobutyronitrile (AIBN) (Shanghai Chemical Reagent Factory, Shanghai China) are directly used without purification. The deionized (DI) water is self-made. The vacuum/pressure equipment is self-made.

Poplar wood (Populus ussuriensis Kom) veneers, with size of 1200 mm × 600 mm × 2 mm (Length × Width × Height), were brought from the Maoershan plantation in the Heilongjiang province of China. Wood samples with different sizes for property evaluation were cut from the above wood veneers and oven-dried at 105 °C for 24 h, and then stored for further use. The even density of the wood samples after oven-dried treatment was 0.33 ± 0.03 g/cm³. All samples showed no defects, such as knots and nodules.

Medium-density fiberboard (MDF) with a size of 300 mm \times 300 mm \times 18 mm (Length \times Width \times Height), a density of 0.68 g/cm³, and a particleboard with a size of 300 mm \times 300 mm \times 300 mm \times 16 mm and a density of 0.72 g/cm³, and plywood with a size of 300 mm \times 300 mm \times 9 mm (Length \times Width \times Height) were all produced by the NanCha Artificial Board Factory (Yichun, China).

2.2. Experimental Methods

2.2.1. Sample Preparation Methods

The active monomers with different formula (see Section 3.1.2), and AIBN accounting for 1 wt.% of the total mass of the monomer solution, were mixed and stirred at 300 rpm to form a uniform solution under room condition; and then the solution was immersed into the poplar veneers (300 mm \times 300 mm \times 2 mm) under the conditions of pressure of -0.08 MPa for 10 min, followed by pressure of 0.8 MPa for 10 min. After pressure relief, the excess liquid on the surface of the veneers were wiped off by filter papers, and then put on the three wood-based panels (MDF, particleboard, and plywood) for hot pressing, according to the designed formula with different hot pressing parameters, including temperature, pressure, and time (see Section 3.1.2). The aimed veneered, wood-based panel composites were finally derived after that, and sawed into different sizes for property evaluation.

2.2.2. Characterization and Property Evaluation of the Composites

- (1) SEM characterization: Slice samples with a size of 0.3 cm × 0.6 cm × 0.3 cm (R × T × L) were cut from the profile side of the composites using a blade, and then fixed onto the loading platform with adhesive tape, sprayed by vacuum-gold-sputtering instrument; and the bonding interface between the veneer and the panel were further observed by the scanning electron microscope (ESEM, QUANTA2000, FEI Inc., Hillsboro, OR, USA), under conditions of high vacuum mode, a working voltage of 12.5 kV, and a beam spot of 5.0.
- (2) The bonding strength of the composites was evaluated according to the standard of "Surface Decorated Wood-Based Panels" (GB/T 15104-2006). The surfaces of the samples, with a profile size of 50 mm × 50 mm, were glued by thermoplastic adhesive onto two steel plates, and the bonding strength between the veneer and the wood-based panel was measured by the universal testing machine (AG-10TA, Shimadzu Corporation, Japan). Three parallel tests were conducted to evaluate the bonding strength.
- (3) The hardness, abrasion resistance, modulus of rupture (MOR), and modulus of elasticity (MOE) were determined by the standard of "Test Methods of Evaluating the Properties of Wood-based Panels and Surface Decorated Wood-Based Panels" (GB/T 17657-2013). The samples for hardness evaluation were cut into a size of 50 mm × 50 mm × 20 mm (R × T × L). The samples for abrasion resistance evaluation were cut into a size of 100 mm × 100 mm × 20 mm (R × T × L). The samples

for MOR and MOE evaluation were cut into a size of 20 mm \times 20 mm \times 300 mm (R \times T \times L). Three parallel tests were conducted to evaluate each of the above property.

Noting that the veneer was just 2 mm in thickness—thinner than the standard demand of indentation depth of 5 mm for hardness evaluation—the study tested the pressure value when the indentation depth was 1 mm, which was converted into the standard value with a demand of 5 mm depth for hardness evaluation.

The abrasion resistance was evaluated by measuring height loss of the veneer-decorated wood-based panel composite after its surface was abraded by the grinding wheel of the abrasion testing machine (MMG-5A, Jinan Tianchen Testing Machine Manufacturing Co., Ltd., Jinan, China), for 1000 rotations.

The MOR and MOE were evaluated by the three-point bending method, according to the GB/T 17657-2013 [31,32]. In brief, the sample was put on two support points of the hot press (Harbin Dongda Artificial Board Machinery Manufacturing Co., Ltd., Harbin, China) with a full range of 100 tons and a hot-pressing area of 420 mm \times 420 mm. Then, the fixed loading was applied onto the middle of the sample, which made the sample bent. The MOR and MOE values were finally obtained when the sample became disrupt at the middle.

Water resistant test: The end-matched sample size was 20 mm \times 20 mm \times 2 mm (R \times L \times T). The samples were immersed in distilled water for different durations, and the corresponding weights of the samples, before and after water absorption were also tested. The water resistance was evaluated based on the reduction in water absorptivity (RWA). Five samples were tested for the mean value.

The RWA was calculated as follows:

$$RWA (\%) = 100 \times (WAu - WAt)/WAu$$
(1)

where WAt and WAu is the water absorptivity of the treated and untreated wood, respectively. The WA was defined as follows:

$$WA (\%) = 100 \times (W1 - W0)/W0$$
(2)

where W1 and W0 are the samples' weight after and before immersion, respectively.

3. Experimental Results and Discussion

3.1. Optimization of the Active Monomer System Based on the Bonding Strength

Simultaneously realizing the in-situ polymerization and glue bonding by the active monomers is the key to realize the structural design of the composite. Therefore, this study attempted to determine the optimal reaction ratio of the active, hot pressing process conditions and catalyst content, in terms of taking the surface bonding strength of veneer composite as an index, so as to lay a foundation for the subsequent evaluation of the comprehensive performance of the target material.

3.1.1. Optimization of the Monomers Ratio of GMA and EGDMA

The literature reports that reaction of the epoxy group and hydroxyl group could occur in the temperature range of 110–130 °C [29,30,33–39]. Considering the hot pressing conditions of the melamine-impregnated paper, glue-bonding wood-based panels, this study preliminary designed a hot pressing temperature of 130 °C, a pressure of 0.8 MPa, and a duration of 15 min, and explored the monomer reaction ratios in terms of the bonding strength between veneer and wood-based panel. Three traditional wood-based panels (particleboard, fiberboard, and plywood) were employed for the experiment study. The results are shown in Figure 1.



Figure 1. Optimization of the monomers reaction ratio of the three wood-based panel composites: (a) The veneer-decorated particleboard composite; (b) the veneer-decorated fiberboard composite; (c) and the veneer-decorated plywood composite.

It can be seen from Figure 1a that when the molar ratio of GMA:EGDMA was 1:1, the bonding strength of the veneer-decorated particleboard composite was 0.35 MPa, which was less than the standard value of 0.40 MPa; while its bonding strength was higher than the standard value when the molar ratio of GMA:EGDMA was greater than or equal to 2:1, and the bonding strength increased with the ratio. Similar trends also appeared in two other wood-based panel composites (Figure 1b,c). The only difference was that the bonding strength of both composites was, respectively, higher than the standard value even when their monomers ratio was 1:1.

Considering the molecular structure of the monomers, the above results could be explained as follows. The epoxy equivalent (the proportion of epoxy groups in the total molecular weight of monomers) increases with the molar ratio of GMA:EGDMA, which theoretically increases the probability of the chemical reaction of the monomers and wood hydroxyl groups. Thus, the corresponding bonding strength between the veneer and the wood panel increased with the monomers ratio. However, the three wood-based panels presented different surface roughness, which had a significant impact on the surface bonding strength. In total, the rougher the surface of the substrate, the smaller the contact area between the veneer and the wood panel, lower the bonding strength. Generally, the surface roughness of the three kinds of wood-based panel are ranked as follows—particle board > medium density board > plywood, thus, their corresponding composites present increased bonding strength at the same monomers ratio.

It is noteworthy that the bonding strength of the veneer-decorated particleboard composite was lower than the standard value when the monomers ratio was less than 2:1. In order to easily compare the bonding strengths of the three kinds of composites, and considering the cost of the monomers (GMA is more expensive than EGDMA), we determined the monomer ratio of 2:1 (GMA:EGDMA) as the basic condition for the subsequent exploration of the hot pressing process.

3.1.2. Optimization of the Hot Pressing Conditions of the Three Kinds of Composites

The above monomers with a determined molar ratio of 2:1 (GMA:EGDMA), and additional AIBN, which accounts for 1 wt.% of the total mass of the monomers, were impregnated into the veneer by the vacuum-pressure processes; after that, the veneer was put on the wood-based panels, followed by the hot pressing treatment, during which the monomers realized the in-situ polymerization and glue bonding. Thus, we finally obtained the modified veneer-decorated wood-based panel composites. The optimal hot pressing conditions were determined by testing the bonding strength of the composites.

The above experimental process was listed as follows—configuration of the optimized monomers solution \rightarrow impregnating veneer \rightarrow lay-up of veneer and panel \rightarrow hot pressing \rightarrow aimed composite \rightarrow testing of the bonding strength.

According to the reaction-active temperature range of GMA, combined with the conventional hot pressing pressure and the time of melamine-impregnated paper, the experiment was designed into an orthogonal test with three factors and three levels, as follows—hot pressing temperature at three levels—110 °C, 120 °C, and 130 °C; hot pressing pressure at three levels—0.5 MPa, 0.65 MPa,

and 0.8 MPa; and hot pressing time at three levels—9 min, 12 min and 15 min. The results are shown in Figure 2.



Figure 2. Optimization of the hot pressing conditions of the three kinds of composites: (a) The veneer-decorated particleboard composite; (b) the veneer-decorated fiberboard composite; and (c) the veneer-decorated plywood composite.

Figure 2a indicated that for the veneer-decorated particleboard composite, the bonding strength from formula 6 (130 °C, 0.65 MPa and 9 min) was the highest, while the value of formula 5 (120 °C, 0.5 MPa and 15 min) was the lowest; only formula 6 and formula 2 derived effective results that were higher than the standard value of 0.4 MPa. Depending on the range analysis of factor significance, we got a descending order of three factors as hot pressing temperature > hot pressing pressure = hot pressing time. Based on the above analysis, the optimized parameters determined were a hot-pressing temperature of 130 °C, and a hot-pressing pressure of 0.50 MPa, and a hot-pressing duration of 9 min.

Figure 2b indicated that for the veneer-decorated fiberboard composite, the bonding strength from formula 9 (130 °C, 0.5 MPa, and 15 min) was the highest, while the value of formula 7 (110 °C, 0.65 MPa, and 9 min) was the lowest; only formula 4, 5, and 7 derived ineffective results that were lower than the standard value of 0.4 MPa. Depending on the range analysis of factor significance, we got the descending order of the three factors as hot pressing temperature > hot pressing pressure = hot pressing time. Based on the above analysis, the optimized parameters determined were a hot-pressing temperature of 130 °C, and a hot-pressing pressure of 0.50 MPa, and a hot-pressing duration of 15 min.

Similar results of the veneer-decorated plywood composite were also derived from Figure 2c, such that the descending order of the three factors was hot pressing temperature > hot pressing pressure = hot pressing time; and the optimized hot-pressing temperature, pressure, and time was 120 °C, 0.65 MPa, and 15 min, respectively.

In short, the hot-pressing process parameters of the three composites presented the same effect on the their bonding strength, which was the most significant for temperature, followed by pressure and time. The optimized hot pressing conditions of the three composites were 130 °C, 0.50 MPa, and 9 min, for the particleboard composite; 130 °C, 0.50 MPa, 15 min for the fiberboard composite; and 120 °C, 0.65 MPa, 15 min for the plywood composite, respectively.

In this experiment, on the basis of the optimal hot pressing process determined above, maleic anhydride was selected as the ring-opening catalyst for the epoxy group of GMA and the cross-linking curing agent for the C=C group of GMA; and its influences on the bonding strength of the composites were also investigated to determine its optimal dosage. For facilitating comparison among the three wood-based panel composites, the preferred hot pressing condition was determined as 130 °C, 0.65 MPa, and 15 min.

The preparation process was similar to that of Section 2.2.1. The only difference was the addition of MAN into the monomers. The MAN content, accounting for the monomers weight, was designed to be 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, 5 wt.%, and 6 wt.%, respectively. The results of the bonding strength are shown in Figure 3.



Figure 3. Optimization of the maleic anhydride (MAN) content of the three wood-based panel composites—(a) the veneer-decorated particleboard composite; (b) the veneer-decorated fiberboard composite; and (c) the veneer-decorated plywood composite.

It can be seen that with the increase of MAN content from 1 wt.% to 6 wt.%, the bonding strength of the veneer-decorated particleboard composite basically presented an increasing trend, indicating an obvious function of the MAN as the catalyst (Figure 3a). Analyzing from the perspective of the molecular structure, MAN has a cyclic anhydride group, which could not only occur as an esterification reaction with a wood hydroxyl group and a GMA epoxy group, but also undergo in-situ polymerization with the C=C bonds from the monomers; consequently, it can theoretically improve the reaction of the epoxy group and the wood hydroxyl group, and also reinforce the polymer networks by the cross-linking reaction of the C=C bonds, which improve the "glue bonding" function of the monomers system between the veneers and the wood-based panels. Thus, the above result could be easily understood, such that the bonding strength increased with the MAN addition.

Similar results were also shown in the veneer-decorated fiberboard (Figure 3b) and plywood (Figure 3c) composite, such that the bonding strength increased with the MAN content and reached a maximum value at the MAN content of 6 wt.%. It is noteworthy that comparing the bonding strengths of the three composites, these were ranked in descending order as plywood composite, fiberboard composite, and particleboard composite, which was consistent with the above results. In short, given the total results, the optimal MAN content was determined as 6 wt.% of the whole monomers.

3.2. Properties Evaluation and SEM Characterization of the Optimized Composites

3.2.1. Properties Evaluation of the Optimized Composites

The three optimized composites were prepared under the consistent conditions—the monomer ratio of GMA:EGDMA was 2:1 (molar ratio); and the MAN content was 6 wt.%; and the hot pressing temperature, pressure, and time was 130 °C, 0.65 MPa, and 15 min, respectively. For comparison, the unmodified veneer-decorated wood-based panel composites were also prepared by white latex adhesive under room temperature with a pressure of 0.65 MPa for 24 h. The bonding strength, hardness, abrasion resistance, and MOR of all composites are shown in Table 1.

Table 1. (Comparison of	the surface properti	es of all the veneer-	decorated wo	ood-based par	el composites [ª].
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Wood Recod Densis	Particleboard Composite		Fiberboard Composite		Plywood Composite	
Properties	Unmodified Veneer	Modified Veneer	Unmodified Veneer	Modified Veneer	Unmodified Veneer	Modified Veneer
Hardness (N)	833	1125	833	1185	833	1262
Abrasion Resistance (mm)	1.25	0.89	1.25	0.98	1.25	0.91
		0.73		0.81		1.09
Bonding Strength (MPa)	—	(Standard		(Standard		(Standard
		Value ≥ 0.4)		Value ≥ 0.4)		Value ≥ 0.5)
Modulus of Rupture (MPa)	11.51	13.52	14	16.76	—	_

^a Each value was obtained from three parallel tests.

It was observed that the surface hardness of the modified veneer-decorated wood-based panel composite increased by 35% (particleboard composite), 42% (fiberboard composite), and 51% (fiberboard composite), compared to the control, respectively; and the abrasion resistance was improved 28%, 22%, and 27%, respectively. The MOR was 15% (particleboard composite) and 16% (fiberboard composite) higher than that of the control, respectively; and their bonding strengths were significantly higher than their standard values. The property differences among the composites presented the same trends as above.

Figure 4 presents the variation trends of the reduction in water absorptivity (RWA) of the modified and unmodified wood veneer within a water immersion time of 200 h. The RWA value of the modified veneer slightly increased from ~4% to ~20%, within the whole immersion time, while that of the unmodified veneer significantly increased from ~50% to ~130% within the whole time, which indicated that the modified-veneer obtained significantly improved water resistance.



Figure 4. Comparison of the reduction in water absorptivity (RWA) of the unmodified wood (black curve) veneer and the modified wood veneer under the optimized monomers system (red curve).

In total, the remarkably improved hardness, abrasion resistance, MOR, bonding strength, and water resistance of the above composites, which were comparable to those of the melamine-impregnated paper (GB/T 15104-2006), indicated that the modified veneer was preferred to replace the paper to be applied to decorate the wood-based panels.

3.2.2. SEM Characterization of the Optimized Composites

Figure 5 shows the SEM morphologies of the cross-section of the three composites. It was clearly found that the bonding interfaces of all three composites were tightly combined without obvious interfacial gaps, indicating that the active monomers realized glue bonding of the veneer and the wood-based panels during their in-situ polymerization within veneer, thereby, endowing the composites with a good bonding strength between the veneer and the panels, which was consistent with the above research results.















(e)



(**f**)

Figure 5. The digital photos (**a**,**c**,**e**) of the three modified veneer-decorated wood-based panel composites and their SEM morphologies of the bonding interface (**b**,**d**,**f**). The digital photo (**a**) of the modified veneer-decorated particleboard composite and the SEM morphology of the bonding interface (**b**). The digital photo (**c**) of the modified veneer-decorated fiberboard composite and the SEM morphology of the bonding interface (**d**). The digital photo (**e**) of the modified veneer-decorated plywood composite and the SEM morphology of the bonding interface (**f**).

4. Conclusions

In this study, we prepared the modified veneer-decorated wood-based panel composites through the hot pressing method, via simultaneous in-situ polymerization and glue bonding of the monomers. The optimized preparing crafts of the composites were determined such that the molar ratio of glycidyl methacrylate (GMA)—ethyleneglycol dimethacrylate (EGDMA) was 2:1, the amount of maleic anhydride (MAN) was 6 wt.% (percentage of total monomers weight), and the hot pressing conditions were temperatures of 130 °C, pressure of 0.65 MPa, and duration of 15 min.

Under the optimized preparations, the three derived composites presented an improved hardness of 35% (particleboard), 42% (MDF), and 51% (plywood); improved abrasion resistance of 28% (particleboard), 22% (MDF), and 27% (plywood); and improved MOR of 15% (particleboard) and 16% (fiberboard) over the corresponding unmodified veneer-decorated composites, respectively. Additionally, all three composites obtained good bonding strengths, which were all significantly higher than the standard demanding values. The water resistance of the modified veneer was also significantly improved by this method. The SEM observation proved the excellent bonding strength, such that the interface between the veneers and the panels was closely interacted without obvious gaps.

Author Contributions: X.Y., X.D. (Xiaoying Dong), Y.D., and Y.L. designed the experiment. X.Y., D.X., and Y.S. performed the whole experiments. Y.G. and J.F. drew the figures. X.D. (Xiaoying Dong) and J.F. carried out the performance evaluations. D.X., J.F., Z.H., X.D. (Xiaohan Dai), and Y.L. wrote the paper. Everybody commented on the final manuscript. All authors have read and agreed to the published version of the manuscript.

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