Processing Variable Optimization of Plywood Hot Pressed with Ba^{2+}-Modified Phenol-Formaldehyde Resin by a Response Surface Method

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Abstract

$Ba(OH)_2$ was added in the synthesis of phenol-formaldehyde resin to realize a low-temperature and fast-bonding process for plywood production. Plywood bonding was investigated by studying a number of parameters, such as the glue spread, the amount of curing agent, and the temperature and duration of the hot-pressing process. The plywood bonding strength was characterized by the shear strength of the adhesive layer, and a mathematical model describing the process and the response was developed using a central composite design and response surface methods. The variance analysis revealed that the newly developed model was reliable, with a high signal-to-noise ratio. All the factors and their interactions were analyzed to optimize the bonding process. Thus, seven optimized processes were obtained from the model, and the optimal process conditions were revealed (glue spread: 277.8 g/m^2; amount of curing agent: 3.5%; hot-pressing temperature: 108°C; and hot-pressing duration: 34.99 s/mm). The results from repeated average shear strength experiments of five veneer testing samples (1.64 MPa) verified the reliability of the optimized technics.

Phenolic resins are widely used in the wood-based panel industry because of their high bonding strength and water-, aging-, and heat-resistance characteristics (Junliang and Zehui 2002). However, phenolic resins suffer from high curing temperatures and low curing speeds, thereby requiring high hot-pressing temperatures and long hot-pressing durations (Christjanson et al. 2010) to maximize quality. However, these treatments result in high energy consumption and low production efficiency, which are problems that affect the application of these resins that should be addressed. The utilization of high-ortho catalysts, monomer embedment, and curing agents allow the curing treatment to be carried out at milder conditions (i.e., lower temperatures) and with higher rates. These methods reduce the energy consumption during wood-based panel production (Pizzi 1979a, Tomita and Hse 1998, Mianwu and Wei 2017, Omar 2017).

Oxides or hydroxides of divalent metal ions are effective high-ortho catalysts. The phenolic hydroxymethyl group at the para position is more reactive than that at ortho position. During the synthesis of phenol-formaldehyde (PF) resins, the addition of divalent metal ions, such as Ba^{2+}, can trigger a complex reaction at the ortho position of the benzene ring via an inductive effect of the electron cloud. Thus, ortho methylation prevails in these processes. The remaining para-hydroxymethyl group undergoes subsequent bonding poly-condensation, which can accelerate the curing speed of the phenolic resin and reduce the curing reaction temperature (Markovic et al. 2001, De Medeiros et al. 2003). The TGA and DTG curves of PF resins that include divalent metal ions and control samples demonstrated that ortho hydroxyl

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methylation is the most dominant reaction in the uncured resin triggered with Ba^{2+} as the catalyst, resulting in a high content of ortho methine linkages, leaving the para position, which has the highest reactivity, unreacted (Chen et al. 2018). The addition of appropriate amounts of a curing agent to the system enables a feasible approach to achieve low temperature and fast curing processes. The curing agent acts as both a reactant and an intermediate that bridges the phenolic core, this also leading to lower curing temperatures and higher curing rates.

Response surface methodology (RSM) is an efficient process optimization method. Traditional single-factor optimization experiments do not take into account the interaction between multiple factors. While a full factorial experiment can overcome this limitation, this methodology is time consuming (Vitanov et al. 2010). RSM ensures the accuracy of the experiment and reduces the number of experiments required. RSM can be applied to nonlinear matching of experimental results with high predictability (Xie et al. 2012). Since its introduction in the 1950s, RSM has been successfully applied to optimize several processes (e.g., wood-based panel manufacturing; Agrawal et al. 2015, Cicek et al. 2015).

In this study, Ba^{2+} with a phenol content of 0.45 percent was added as a catalyst in the synthesis of phenolic resin, according to investigations on the effect of different divalent metal hydroxide catalysts added at different concentrations on the polymerization rate of PF resin in a previous study (Chen et al. 2018). Subsequently, we added a certain amount of curing agent to the prepared PF resin. The bonding process was optimized by RSM.

Experiment

Chemical reagents, experimental materials and test instruments

All chemical reagents were of analytical grade and included phenol (Guangdong Guanghua Sci-tech Co., Ltd), formaldehyde (37%; Chengdu Kelong Chemical Reagent Factory), Na_2CO_3 (Sinopharm Group), and sodium hydroxide and barium hydroxide (Sinopharm Group Chemical Reagent Co., Ltd). Poplar rotary cutting veneer with dimensions of 300 by 300 by 2 mm was obtained from the Jiangsu Siyang Huayuan Wooden Plate Factory.

An electrothermal drying oven (101-2A; Tianjin Taisite Instrument Co.), a pressing machine (BY302*2/150T; Suzhou Zhuohua Mechanical and Electrical Technology Co. Ltd), and a mechanical testing machine (MWD-W10; Jinan Shijin Testing Machine Group Co. Ltd) were used for our experiments.

Synthesis of PF resin and gluing

NaOH (32 g) was dissolved in water (74.67 g), cooled to room temperature, and transferred to a four-neck boiling flask. Next, the NaOH solution was mixed with 188.22 g of melted phenol while the temperature was maintained below 50°C with a water bath. $Ba(OH)_2$ was added to this solution at 0.6 percent of the total mass of phenol. Formaldehyde (324.64 g) was then added after the reaction proceeded for 20 minutes. The temperature was held at 60°C for 50 minutes before it was increased and held at 90°C for about 45 minutes. Once the viscosity was up to 300 mPa/s, the reaction was regarded as completed.

Na_2CO_3, as the curing agent, was added to the above-mentioned PF resin. For making a three-layer poplar experimental veneer, the produced resin was applied evenly on one side of two poplar veneers. The glue spread was controlled by measuring the weight of the sheets before and after the process. The sheets were placed into an electrothermal drying oven, and the temperature was closely monitored to prevent precuring. Once the surface was dry, the sheets were assembled one on top of another such that the grains of the adjacent surfaces were vertical to each other and were subsequently placed into the pressing machine along with the press plate. Hot pressing was carried out according to the preset process parameters, and the plate was subsequently unloaded, cooled down, and assembled. The test pieces were cut according to the Chinese national standard GB/T9846.7-2004 (Standardization Administration of the People's Republic of China [SAC] 2004).

The hot-pressing process mainly included the following parameters: hot-pressing temperature, hot-pressing duration, hot-pressing pressure, and initial water content. Among them, the factors affecting the bonding strength to a greater extent were the hot-pressing temperature and the hot-pressing duration, and these were the independent variables primarily investigated in this article. The curing accelerator showed a direct effect on the design of the process parameters. At the same time, this factor greatly influenced the shear strength of the adhesive layer also included in the glue spread. Therefore, the hot-pressing temperature, hot-pressing duration, curing agent, and glue spread were tested at various low and high levels (Table 1). The central composite design method was adopted, and the design expert software was used to carry out the experimental design (Table 2). Each process was configured and set according to the level of the experimental design.

Bonding performance test

The bonding performance of the as-prepared wood-based panels was evaluated by applying a tensile (compressive) load to produce shear damage to the adhesive layer of the test pieces. The bonding performance is usually determined by how much substrate is present, the interface, and the adhesive layer. In the case of the interface bonding performance, a certain wood failure ratio is ensured and can be regarded as an effective bonding (i.e., bonding strength greater than the mechanical strengths of the substrate and the adhesive layer). The mechanical properties of the substrate remained constant for the conventional materials and were not considered here. Therefore, the capability of the material layer to withstand shear forces is usually considered as the bonding properties. The test piece was pretreated using the boil-dry-boil process according to section 4.17 of the GB/T17657-2013 standard (SAC 2013), and the shear strength of the adhesive layer was tested on the mechanical testing machine according to the method in section 4.18 of the GB/T17657-2013 standard (SAC 2013).

Results and Analysis

Experimental results

Four factors that have a significant influence on shear strength of plywood were selected: glue spread (A), curing agent (B), hot-pressing temperature (C), and hot-pressing duration (D). Response surface analysis tests of four factors

Table 1.—Factors and levels of response surface analysis.

Factor	Name	Units	Min	Max	Coded	Values	Mean
A	Glue spread	g	10	50	−1.000 = 20.00	1.000 = 40.00	30
B	Curing agent	%	0	8	−1.000 = 2.00	1.000 = 6.00	4
C	Hot-pressing temperature	°C	100	120	−1.000 = 105.00	1.000 = 115.00	110
D	Hot-pressing duration	s/mm	15	75	−1.000 = 30.00	1.000 = 60.00	45

and three levels were conducted (Chen et al. 2018); the factor levels of the experimental design optimization using RSM and the experimental results are shown in Table 2. The ratio of the absolute average value of the test results was smaller than 3, which proved that the preliminary technical parameters were optimal.

Quadratic response surface fitting

After the initial fitting, redundant insignificant terms were found, and backward elimination regression was conducted to delete the terms with an A value higher than 0.1 to improve the model. The coded model about the response value (i.e., coded shearing strength) was

$$\mathrm{RVcod} = +1.77 + 0.11\mathrm{A} - 0.025\mathrm{B} + 0.13\mathrm{C} - 0.014\mathrm{D} - 0.26\mathrm{BC} - 0.13\mathrm{CD}$$

After substitution with the actual step sizes, the quadratic response surface fitting of the actual terms (i.e., actual response value) was obtained as follows:

Table 2.—Design of the response surface experiments and results.

Std[a]	Run	A	B	C	D	Shearing strength (MPa)
3	1	20	6	105	30	1.48
18	2	50	4	110	45	1.78
24	3	30	4	110	75	1.63
25	4	30	4	110	45	1.64
21	5	30	4	100	45	1.56
13	6	20	2	115	60	2.04
17	7	10	4	110	45	1.62
5	8	20	2	115	30	1.8
6	9	40	2	115	30	2.46
23	10	30	4	110	15	2.06
11	11	20	6	105	60	2.08
22	12	30	4	120	45	2.18
15	13	20	6	115	60	0.9
19	14	30	0	110	45	1.62
7	15	20	6	115	30	1.84
9	16	20	2	105	60	1.6
14	17	40	2	115	60	2.1
26	18	30	4	110	45	1.92
29	19	30	4	110	45	1.88
4	20	40	6	105	30	2.06
20	21	30	8	110	45	1.05
28	22	30	4	110	45	1.7
30	23	30	4	110	45	2
12	24	40	6	105	60	2.08
10	25	40	2	105	60	1.4
8	26	40	6	115	30	1.76
27	27	30	4	110	45	2.34
2	28	40	2	105	30	1.25
1	29	20	2	105	30	1.08
16	30	40	6	115	60	2.06

[a] Std = standard order.

$$\mathrm{RVact} = -16.2837 - 0.1671\mathrm{A} + 2.8442\mathrm{B} + 0.1617\mathrm{C} + 0.1956\mathrm{D} + 0.0030\mathrm{AB} + 0.0016\mathrm{AC} - 0.0001\mathrm{AD} - 0.026312\mathrm{BC} - 0.0012\mathrm{BD} - 0.0017\mathrm{CD}$$

According to Tables 3 and 4, the model F value of 2.41 showed that the model was significant. There was only a 4.72 percent chance that a model F value this large could occur due to noise. Additionally, the P value showed that the lack of fit was 0.288, which was considered not statistically significant (i.e., higher than 0.05). These results revealed the good significance of the model. The adjusted R^2 value was 0.328, in line with the predicted R^2 value (0.336). The signal-to-noise ratio (adequate precision, 6.648) was higher than the general requirement of 4, thereby revealing that the signal was sufficient. In this case, C and BC were the significant model terms for the values being greater than 0.100, which is consistent with the low-temperature bonding effect of divalent metal ions and rapid curing influence of curing agents (Chen et al. 2018).

Since the response surface model assumes that the error has a zero mean, a residual analysis was performed. A systematic error (constant error) test, outlier detection, and variable transformation analysis were also carried out to ensure that the model was correct and suitable.

As shown in Figure 1, the residuals were evenly distributed on both sides of the straight line, and the regression model was well fitted to meet the normality requirements. Therefore, the correctness of the fitting function can be determined, as shown in Figure 2. The residuals were evenly distributed across the 0 axis, satisfying the assumption that the error of the model had a zero mean, proving that the model is credible and effective.

Table 3.—Analysis of variance results for the response surface reduced 2 factors interaction (2FI) model.

Source	Sum of squares	df	Mean square	F value	P value prob > F
Model	2.289	10	0.229	2.414	0.047 significant
A (glue spread)	0.297	1	0.297	3.133	0.093
B (curing agent)	0.016	1	0.016	0.164	0.691
C (hot-pressing temperature)	0.419	1	0.419	4.416	0.049
D (hot-pressing duration)	0.005	1	0.005	0.048	0.829
BC	1.108	1	1.108	11.683	0.003
BD	0.020	1	0.020	0.214	0.649
CD	0.263	1	0.263	2.770	0.112
Residual	1.802	19	0.095		
Lack of fit	1.491	14	0.106	1.712	0.288 not significant
Pure error	0.311	5	0.062		
Cor total	4.091	29			

Table 4.—Model summary statistics.

Source	SD	R^2	Adjusted R^2	Predicted R^2	Press
Linear	0.366	0.180	0.049	−0.228	5.024
2FI	0.308	0.560	0.328	−0.335	5.463 suggested
Quadratic	0.291	0.689	0.398	−0.464	5.989
Cubic	0.291	0.855	0.398	−9.075	41.211 aliased

Figure 3 was used to detect the outliers, where scattered points lying outside of the red line were considered outliers. No outliers were found herein, so the test samples were accurate and did not need to be removed.

The need for variable transformation was analyzed in Figure 4. As shown in Figure 4, no transformation was recommended in the model.

In summary, this quadratic response surface fitting model was appropriate for this process. The final model can be determined:

$$\begin{aligned}\text{RVact} = {} & 16.2837 - 0.1671\text{A} + 2.8442\text{B} + 0.1617\text{C} \\ & + 0.1956\text{D} + 0.0030\text{AB} + 0.0016\text{AC} \\ & - 0.0001\text{AD} - 0.026312\text{BC} - 0.0012\text{BD} \\ & - 0.0017\text{CD}\end{aligned}$$

Analysis of various factors and their interactions

The analysis of variance (Table 3) showed that Factor C and the interaction between B and C were the main parameters affecting the bonding strength. Some interactions existed among Factors B, C, and D, although they were not suitable for single-factor analysis. As shown in Figure 5, the internal bonding strength increased with Factor A (glue spread). Sufficient adhesive infiltration is required to achieve bonding strength. An increase in glue spread resulted in adhesive penetration during the test, and this can explain the increase in the bonding quality.

The bonding strength increased with the amount of curing agent (Figs. 6 and 7). This result can be explained by the high activity of the PF resin, which formed a network structure at the traditional hot-pressing temperature (150°C). However, in order to achieve relatively low-temperature

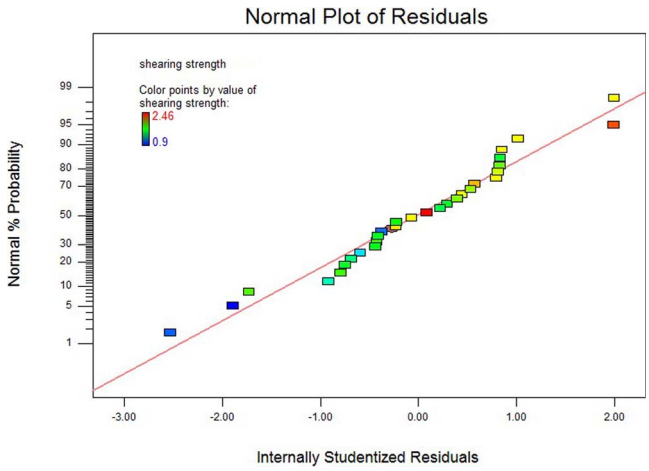

Figure 1.—Normal plot of the residuals.

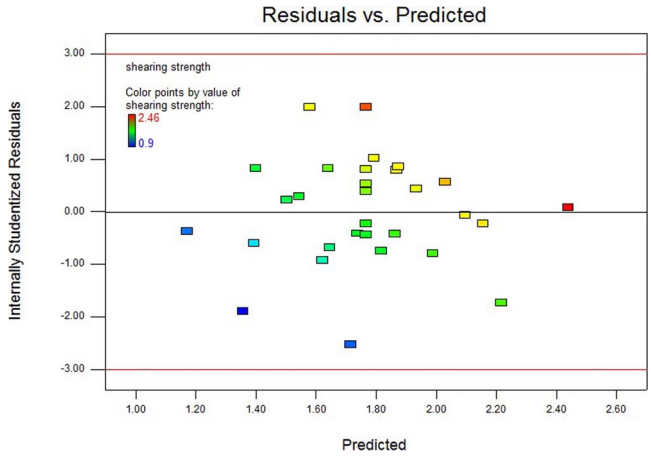

Figure 2.—Residuals versus predicted values.

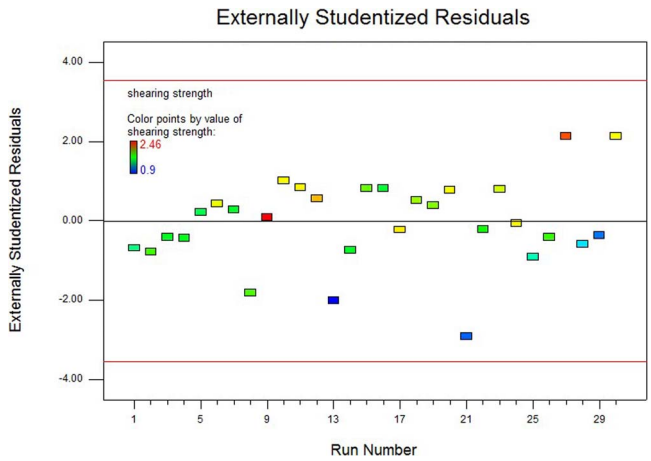

Figure 3.—Externally studentized residuals.

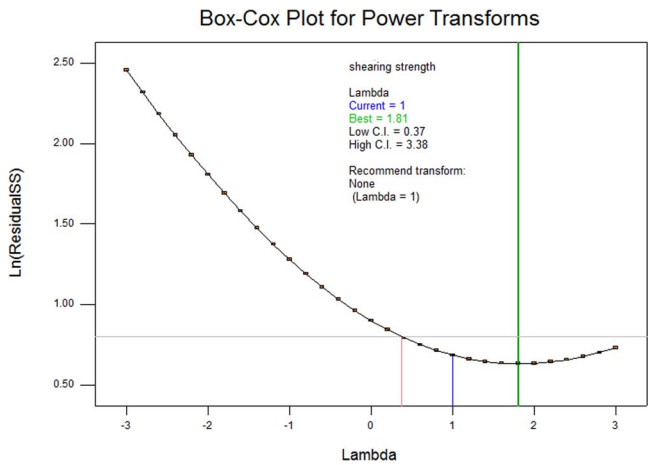

Figure 4.—Box-Cox plot for the power transformations.

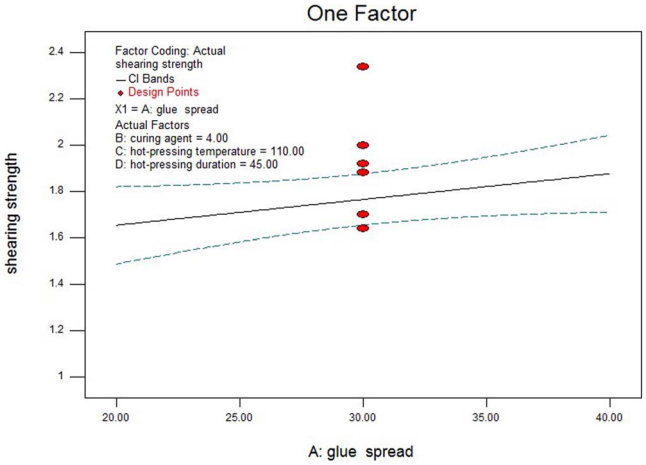

Figure 5.—Influence of Factor A on the shearing strength.

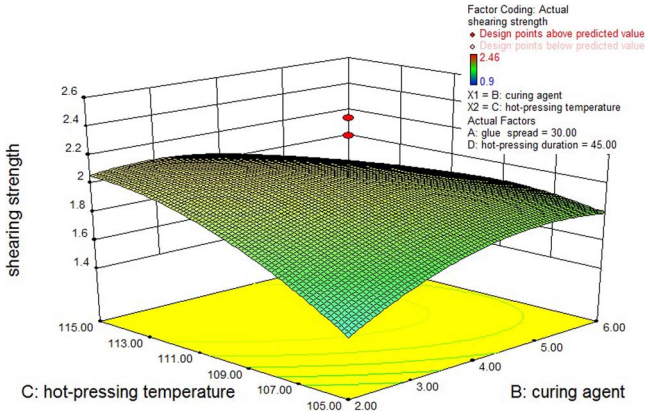

Figure 6.—3D surface on B versus C.

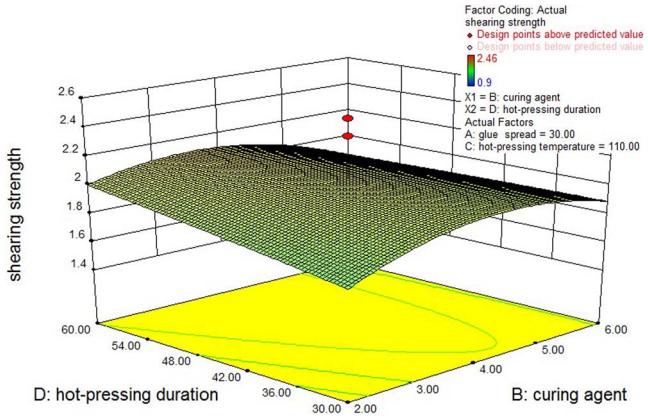

Figure 7.—3D surface on B versus D.

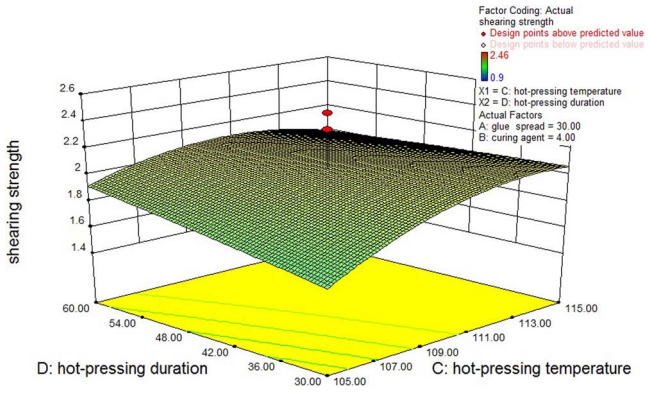

Figure 8.—3D surface on C versus D.

conditions and to accelerate adhesive curing, the curing agent is required to play a catalytic role in the resin polycondensation phase. Nevertheless, according to the above-mentioned single-factor experiment designed by RSM, when the curing agent (Na_2CO_3) was added at levels above 8 percent compared with the amount of PF resin, the reaction was difficult to control, and the active duration was greatly reduced.

The bonding strength remained nearly unchanged with the hot-pressing duration (Figs. 7 and 8). Although the curing speed of the modified PF resin increased, in theory, the plate could be unloaded when the curing rate reached at 70 percent. However, the duration of the hot-pressing process should be above a threshold value, and sufficient heat transfer must be ensured. Thus, the hot-pressing duration should be determined based on a combination of the initial moisture content of the veneer, the target product, and other actual conditions.

The bonding strength increased slowly with the hot-pressing temperature (Figs. 6 and 8), and curing was achieved at 110°C for the modified resin. However, an additional amount of heat was required to evaporate water. The duration of the hot-pressing process can be reduced by increasing the relative hot-pressing temperature such that the interaction between the hot-pressing temperature and the hot-pressing duration increases.

Discussion

According to Table 5, seven optimized processes can be obtained (Table 6). Process 1 could provide the maximum shear strength and was cost effective. In the seven optimized processes, the hot-pressing temperature was 108°C, indicating that the barium ion had a significant effect on the modification of phenolic resin at low temperatures; the cured plywood had excellent shear strength at this temperature. The experiment was repeated in order to verify the reliability of this optimized technique. The average shear strength of the five poplar veneer testing samples (1.64 MPa) was consistent with the value anticipated by the model (1.62 MPa). The results showed that the application of modified PF resin with Ba^{2+} not only can reduce bonding temperature to save energy but also can decrease the bonding time to improve productivity and efficiency. The ortho substitution was induced via the

Table 5.—Constraints of optimization.

Name	Goal	Lower limit	Upper limit
A (glue spread)	In range	22	25
B (curing agent)	In range	3	3.5
C (hot-pressing temperature)	In range	105	108
D (hot-pressing duration)	In range	33	35
Shearing strength	Maximize	1.5	1.8

Table 6.—Optimized technological parameters.

No.	Glue spread	Curing agent	Hot-pressing temperature	Hot-pressing duration	Shearing strength	
1	25.00	3.50	108.00	34.99	1.62	selected
2	24.36	3.50	108.00	35.00	1.62	
3	25.00	3.32	108.00	35.00	1.62	
4	24.09	3.50	108.00	33.00	1.61	
5	24.67	3.00	108.00	35.00	1.60	
6	23.30	3.48	108.00	33.00	1.60	
7	22.62	3.25	108.00	33.00	1.59	

complexation of Ba^{2+} to the oxygens of phenol and formaldehyde, positioning the electrophile for attack by the newly formed negatively charged dipole on the phenol ortho position. During formation of b-stage resin, a dominant reaction occurs between two equivalents of the thus formed methylol phenol with itself to form a longer-chain methylol phenolic that has an ortho-ortho substituted methine bridge. Alternatively, two equivalents of methylol can be dehydrated to the corresponding dibenzyl ether, which can undergo rearrangement to an ortho-ortho methine bridged product equivalent to that formed by the reaction of methylol and phenol (Pizzi 1979b). The remaining phenolic ortho positions can react during the curing process, thereby increasing the polymerization rate of PF resin in the metal-catalyzed reaction, reducing the curing temperature, and accelerating the curing speed during the bonding process of wood-based panels.

Conclusions

The conditions of Process 1 were as follows: A: glue spread = 25 g/side (i.e., 277.8 g/m^2); B: amount of curing agent = 3.5 percent (mass ratio); C: hot-pressing temperature = 108°C; and D: hot-pressing duration = 34.99 s/mm. This optimized process of hot pressing can save energy and reduce the consumption of materials in the wood-based panel industry, which is beneficial to green manufacturing. Meanwhile, this process can also be applied to high-temperature, sensitive materials, such as dyed bamboo or wood, to improve the quality stability of products. Meanwhile, the findings also revealed that RSM can be used to optimize the low-temperature and fast curing bonding process of PF resin in an efficient and feasible manner.

Acknowledgments

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