Dimensional Stability Improvement of Corn Stalk Biocomposites Using Two-part Lignin-derived Binder Optimized with Response Surface Methodology

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To strengthen the dimensional stability of enzymatically treated corn stalk (ECS) biocomposites, hybrid modified lignosulfonate (HML) was used as a binder to fabricate reinforced ECS/HML composites with evaluation by response surface methodology. The effects of the preparation treatment on the enzymatic conditions, as well as the modified lignosulfonate dosage on the physicomechanical properties of the ECS/HML composites, were all evaluated. The optimum preparation parameters were determined *via* the Box-Behnken experimental design. High mass concentrations of laccase-vanillin and an appropriate modified lignosulfonate dosage for a relatively short enzymatic pretreatment time led to reduced residual stresses and improved dimensional properties. The optimum conditions that minimized thickness swelling (TS) and water adsorption (WA) without significantly compromising the biocomposite mechanical properties were determined to be 25 g/L laccase-vanillin, 118.8 min enzymatic pre-treatment time, and 15 wt% modified lignosulfonate. The ECS/HML composites that were treated under the optimal conditions resulted in an approximate 42% reduction in the dimensional properties without any significant decline in mechanical properties when compared to ECS panels. Unlike the loose structure of ECS biocomposites, the ECS/HML composites had a laminar shape with firm morphology.

Keywords: Corn stalk; Enzymatic pretreatment; Hybrid modified lignosulfonate; Box-Behnken design; Physicomechanical properties

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INTRODUCTION

To decrease the emission of toxic volatiles and to protect both the environment and human health, considerable efforts have been devoted to the development of particleboards using natural-derived binders (Widyorini *et al.* 2005a). Such particleboards are biocomposites that are formed without the presence of synthetic resin. It has been shown that their self-bonding strength could be improved by activating the chemical components of board constituents during steam or heat treatment (Widyorini *et al.* 2005b). The main methods employed for this purpose are based on heating or biological treatments (González-García *et al.* 2011; Wang *et al.* 2011, 2013; Wu *et al.* 2011), steam explosion (Xu *et al.* 2004), and combined processes. These approaches are often less hazardous than panel manufacturing with formaldehyde-based adhesives. In addition, bioproducts

prepared without synthetic binders are biodegradable, recyclable, and can be disposed of in environmentally friendly ways (Nadhari *et al.* 2013).

Composite panels can be made of several crops (Thamae *et al.* 2008; Shah 2013), such as corn stalk, wheat straw (Wang and Sun 2002), kenaf core (Xu *et al.* 2003), cotton stalk (Zhou *et al.* 2010), rice husk (Ndazi *et al.* 2006), and castor stalk (Grigoriou and Ntalos 2001). Corn is the most produced cereal worldwide, surpassing wheat and rice (Jarabo *et al.* 2013). The production of corn and its wastes increases each year. Corn residues are industrial raw material sources that can potentially be used in several applications, including human consumption, energy (Yan *et al.* 2012), fuel (Gao *et al.* 2017), carbon materials, and chemical production (Ioannidou *et al.* 2009). The industrial usage of agricultural residues from the forest industry may effectively reduce the production cost, increase the sustainability of the panel manufacturing industry (Juárez *et al.* 2007), and minimize air pollution caused by the combustion of corn residues. However, farmers harvest only the grains, and most of the residues, including the stalks and husks, are burned or disposed of due to several limitations like collection cost and farming conditions (Çöpür *et al.* 2007). For biocomposites, Wu *et al.* (2011) manufactured binderless fiberboards from corn stalk that was pretreated with white-rot fungus. The pretreatment process significantly increased the mechanical properties and improved the crystallinity of the fiberboards without using any synthetic adhesives. However, most binderless biocomposites exhibit deficiencies that limit their industrial applications (Yuan *et al.* 2011). Therefore, the methods for reinforcing the interactions between components are key for improving the physicomechanical properties of biocomposites prepared without synthetic binders.

Lignin significantly affects the manufacturing of binderless biocomposites. Most studies have focused on technical lignin, such as kraft lignin (Velásquez *et al.* 2003; Mancera *et al.* 2011a, 2011b) and lignosulfonate (Jin *et al.* 2011; Ji and Guo 2018; Ji *et al.* 2018), both of which are generated from the papermaking industry. However, the low reactivity of lignin has limited its commercial use; thus it is often discarded or burned to generate energy or recover chemicals. Less than 5% of the world's global lignin supply has been used as low-value compounds (Hu *et al.* 2011). Lignin oxidation with H_2O_2 may effectively improve its safe utilization because water is used to break it down, replacing organic solvents and reducing environmental issues. Alkaline aqueous solutions have been determined to be the best reaction medium compared to acidic or neutral environments (Hu and Guo 2015).

Hybrid modified lignosulfonate (HML) is a type of lignin-based binder with modified ammonium lignosulfonate and polyethylenimine (Yuan and Guo 2014; Yuan *et al.* 2014). Hybrid modified lignosulfonate has a better environmental impact in wood fiber composites because it is a formaldehyde-free binder (Yuan and Guo 2016, 2017). However, only a handful of studies so far have reported on applications related to modified technical lignin in biocomposites using enzymatic treatments. In this study, the feasibility of using HML as a natural binder and enzymatic pretreated corn stalk (ECS) particles as raw materials to manufacture biocomposites was evaluated at a representative factory that had an approximate production capacity of 145,000 m^3/year in Harbin, an urban region in the northeast of China. The Box-Behnken design (BBD) was applied to investigate the effects of variable interactions on the physicomechanical properties of ECS/HML composites. Fourier transform infrared spectrometry (FTIR) and scanning electron microscopy (SEM) were also employed to compare the chemical structures of the binderless biocomposites before and after the introduction of HML.

EXPERIMENTAL

Materials

Corn stalks obtained from Anda (Heilongjiang province, China) were air-dried and stored in jute bags. The corn stalks were chipped through a hacker chipper and then reduced into smaller particles using a knife ring flaker (FW-100 high-speed shredder; HuaYi Instrument Co., Ltd., Changzhou, China). The obtained particles were dried to a moisture content of 5% and passed through 40-mesh to 60-mesh sieve for separation, then stored for the manufacturing of corn stalk biocomposites. The content of ash according to GB/T 742 (2008), ethanol-benzene extractives according to GB/T 10741 (2008), Klason lignin according to GB/T 747 (2003), holocellulose according to GB/T 2677.10 (1995), and α-cellulose according to GB/T 744 (2004) were measured. The hemicelluloses content was calculated by subtracting the cellulose content from the holocellulose content. The average chemical compositions of the initial particles were determined to be 4.6% ash, 14.9% extractives, 16.7% lignin, 45.6% cellulose, and 22.5% hemicelluloses. Due to the overlap in the test parameters, the total chemical composition exceeded 100% (104.4%), which was expected (Angles *et al.* 1997). Ammonium lignosulfonate from Shenyang Xingzhenghe Chemical (Shenyang, China) was used as it was received, with the composition content determined to be 51.9% total lignin, 27.1% carbohydrates, 10.6% ash, and 4.6% moisture. Laccase was purchased from Wuhan Yuancheng Technology Development (Wuhan, China) and stored at -10 °C. The activity of the commercial laccase powder was approximately 4000 U/g. Vanillin (4-hydroxy-3-methoxybenzaldehyde) was purchased from Shanghai Adams Reagent Co., Ltd. (Shanghai, China). Polyethylenimine (PEI) was obtained from Shanghai UN Chemical (Shanghai, China). The molecular weight of PEI was 75,000 in 50 wt% aqueous solution. All other chemicals used were of analytical grade.

Enzymatic treatment of the corn stalks

The corn stalk particles were first pretreated with laccase-vanillin according to previous reports (Yuan and Guo 2013). Briefly, the dried corn stalk particles were suspended in deionized water to yield a 5.0 wt% suspension at a pH of 5, and they were then mixed using a JJ-1 precision-power motor stirrer (Changzhou Wanfeng Instrument Co., Ltd., Changzhou, China). Next, the suspension was stirred with an oxygen stream at temperatures from 45 °C to 47 °C for 180 min. The mass ratio of laccase to vanillin was set to 2.56:100 for 1 L of the desired oxidation system. After the pretreatment, the particles were transferred to gauze for dewatering and were air-dried at 30 °C. They were then dried for 1 h at 100 °C to eliminate enzyme reaction. The target moisture content of the pretreated corn stalk particles was set between 4% and 6%.

Preparation of the HML

Two-part lignin-derived binder was prepared through an oxidation reaction and combination technology using ammonium lignosulfonate (AL) and PEI according to previous reports (Yuan *et al.* 2014). Briefly, 50 g of AL powder was alkalinized in 100 g water adjusted to a pH of 10. Next, 30% H_2O_2 dosage based on dry weight to lignosulfonate was added to the solution. After heating for 30 min at 60 °C, the mixture was concentrated to form a 20 wt% modified ammonium lignosulfonate (MAL) solution. Hybrid modified lignosulfonate was prepared by mixing MAL with PEI at a weight ratio of 7:1 for 30 min.

Manufacturing of the ECS/HML composites

The ECS particles were mixed with HML at different proportions in a SHR-10A high-speed blender (Zhangjiagang Yunfan Machinery Co., Ltd., Zhangjiagang, China). The mixed particles were fixed into the mat of a 250 mm × 250 mm forming box. The target density of all biocomposites was determined to be 0.8 g/cm^3 ± 0.03 g/cm^3 with a target thickness of 5 mm. For reproducibility, each group of experiments under these sets of conditions was replicated three times. The corn stalk biocomposites issued from ECS were prepared and used as controls.

Methods

Physicomechanical properties of ECS/HML composites

For each test, the ECS/HML composites were cut into three test samples according to GB/T 17657 (2013) after conditioning at 20 °C ± 2 °C and 65% ± 5% relative humidity (RH). The test samples were set to 200 mm × 50 mm for the modulus of rupture (MOR) and the modulus of elasticity (MOE) tests, and 50 mm × 50 mm for the internal bonding strength (IB) test. A loading speed of 5 mm/min was selected for the MOR and the MOE tests and 2 mm/min for the IB test. The thickness swelling (TS) and water absorption (WA) were also set to 50 mm × 50 mm using three replicates. The specimens were first immersed in water at 20 °C ± 1 °C and then their thickness and weight changes were measured after 24 h. The load-bearing particleboard properties of GB/T 4897 (2015) were followed as MOR ≥ 15 MPa, MOE ≥ 2.2 GPa, IB ≥ 0.45 MPa, and 24 h TS ≤ 22%.

FTIR and SEM characterization

The FTIR spectroscopy of prepared corn stalks, lignosulfonates, and ECS/HML specimens were characterized using a Nicolet Magna-IR 560 (ThermoFisher Scientific, Madison, USA). The spectra were recorded at wavelengths ranging from 4000 cm^{-1} to 500 cm^{-1}. Each sample was scanned 40 times at resolution of 4 cm^{-1}. Following the IB tests, the SEM results were collected to evaluate the morphological changes of the ECS panels and the ECS/HML composites on a Sirion 200 (FEI Company, Hillsboro, USA) microscope.

Experimental design

A Box-Behnken experimental design with three independent parameters and three various levels was adopted using Design-Expert 8.0.6 software (Stat-Ease Inc., Minneapolis, USA). A total of 17 experiments at a central point were employed to determine the variables that influence the ECS/HML composites' performance. This method allows the establishment of statistical relationships between the experimental variables and response variables to describe the nature of the response surface and elucidate the optimal manufacturing conditions. These features should, in turn, allow for predicting the optimal board properties. Table 1 lists the design matrix and mechanical properties data of the obtained ECS/HML composites.

The three critical parameters that affected the physicomechanical properties of the ECS/HML composites were the mass concentration of laccase-vanillin (X_A), the enzymatic pretreated time (X_B), and the modified lignosulfonate dosage (X_C). These parameters were selected as the independent variables based on preliminary experiments. The dependent variables (response), which include MOR, MOE, IB, 24 h TS, and 24 h WA, were then evaluated. An analysis of variance (ANOVA) was performed for each response at a confidence level of 95%. All data were expressed using the average of three replicates

along with their coefficient of variation (CV). The CV observations for the samples from the ECS/HML composites compared well with those of the control.

Table 1. Experimental Design of Coded Factors and Results of BBD for Physicomechanical Properties of ECS/HML Composites

Coded	Factors					Range and Levels			
						Low (-1)	Medium (0)		High (1)
A	Mass concentration of laccase-vanillin (g/L)					15	20		25
B	Enzymatic pretreated time (min)					120	150		180
C	Modified lignosulfonate dosage (wt%)					10	15		20
Run	Factors			Density (g/cm^3)	MOR (MPa)	MOE (GPa)	IB (MPa)	TS 24 h (%)	WA 24 h (%)
	A	B	C						
1	0	1	-1	0.79	18.47 (4.6)*	1.75 (5.6)	0.50 (5.2)	24.56 (7.4)	30.40 (9.2)
2	0	-1	1	0.82	26.74 (6.2)	2.47 (4.6)	1.16 (5.2)	17.24 (9.2)	21.23 (8.3)
3	0	0	0	0.80	18.90 (5.2)	1.81 (4.8)	0.67 (5.2)	22 (7.9)	28.40 (7.8)
4	1	-1	0	0.83	28.45 (6.3)	3.07 (5.7)	1.24 (5.2)	19.21 (6.4)	22.55 (9.2)
5	0	0	0	0.81	18.20 (5.8)	1.89 (4.2)	0.57 (5.2)	21.75 (6.3)	30.10 (7.1)
6	0	0	0	0.79	19.70 (5.5)	1.80 (6.2)	0.64 (5.2)	18.9 (7.1)	26.90 (8.5)
7	1	0	-1	0.80	24.75 (4.9)	2.94 (3.2)	0.90 (5.2)	20.14 (3.5)	29.10 (7.8)
8	0	0	0	0.81	18.9 (5.4)	2.04 (5.3)	0.67 (5.2)	22.16 (7.4)	28.40 (6.8)
9	-1	0	-1	0.79	10.46 (4.7)	1.09 (3.8)	0.25 (5.2)	35.47 (4.4)	45.63 (8.2)
10	0	1	1	0.82	16.72 (6.7)	1.76 (3.7)	0.46 (5.2)	29.64 (6.2)	30.47 (9.1)
11	1	0	1	0.82	25.74 (5.1)	2.95 (3.4)	1.08 (5.2)	20.23 (7.2)	20.46 (7.5)
12	1	1	0	0.80	26.40 (6.4)	2.48 (4.9)	0.89 (5.2)	18.97 (6.9)	25.64 (7.6)
13	-1	1	0	0.79	22.40 (4.9)	2.39 (4.6)	0.57 (5.2)	24.84 (7.4)	30.4 (8.2)
14	-1	-1	0	0.81	18.74 (5.4)	1.77 (4.6)	0.55 (5.2)	26.47 (7.4)	39.74 (6.2)
15	0	-1	-1	0.79	9.75 (4.8)	0.98 (5.6)	0.30 (5.2)	38.4 (8.5)	45.40 (8.2)
16	-1	0	1	0.82	23.40 (5.3)	2.78 (4.3)	0.74 (5.2)	21.97 (7.4)	27.70 (9.3)
17	0	0	0	0.80	19.40 (5.1)	2.01 (4.6)	0.61 (5.2)	20.32 (9.1)	25.70 (8.2)
Control				0.80	8.93 (6.4)	1.39 (6.7)	0.42 (5.2)	43.25 (8.1)	84.23 (9.1)
GB/T 4897 (2015) load-bearing particleboard					≥ 15	≥ 2200	0.45	≤ 22	-

*Coefficient of variation

RESULTS AND DISCUSSION

Data Analysis and Regression Models

The analysis of variance p-values for the mechanical properties of the ECS/HML composites are presented in Table 2. All p-values below 0.05 revealed significant model terms, while values above 0.05 indicated insignificant model terms (Alslaibi *et al.* 2013). Meanwhile, p-values below 0.0001 would imply that all models of mechanical properties were significant and there is only a 0.01% chance that such values could occur due to noise.

Table 2. Analysis of Variables for p-Value of Parameters and Their Interactions

Response	Model	X_A	X_B	X_C	X_AX_B	X_AX_C	X_BX_C	X_A^2	X_B^2	X_C^2
MOR	< 0.001	< 0.001	0.8836 ns	< 0.001	0.0055	< 0.001	< 0.001	< 0.001	0.0369	0.0007
MOE	< 0.001	< 0.001	0.8313 ns	< 0.001	0.0016	0.0002	0.0005	< 0.001	0.1631 ns	0.2283 ns
IB	< 0.001	< 0.001	0.0003	< 0.001	0.0042	0.0100	< 0.001	0.0002	0.3528 ns	0.0596 ns
TS	< 0.001	< 0.001	0.3740 ns	< 0.001	0.5904 ns	0.0009	< 0.001	0.2092 ns	0.0085	0.0002
WA	< 0.001	< 0.001	0.0152	< 0.001	0.0023	0.0101	< 0.001	0.6949 ns	0.0650 ns	0.0056

ns Not signficant

From the ANOVA results (Table 1), the enzymatic pretreated time levels showed no significant effect on the physicomechanical properties, except for IB and WA. The factors positively affected the physicomechanical properties under different conditions, except for IB that was lower at low-level preparation conditions.

Table 3. Regression Models of Mechanical Properties and Dimensional Stability of ECS/HML Composites

Regression Models	R^2	Predicted R^2	Adjusted R^2	Adequate Precision	Std. dev.
$MOR = 19.02 + 3.79X_A + 3.65X_C - 1.43X_AX_B - 2.99X_AX_C - 4.69X_BX_C + 4.07X_A^2 + 0.91X_B^2 - 2.01X_C^2$	0.9918	0.9112	0.9812	35.458	0.72
$MOE = 1910.62 + 426.52X_A + 400.24X_C - 305.30X_AX_B - 421.58X_AX_C - 371.38X_BX_C + 607.91X_A^2$	0.9827	0.8457	0.9605	23.333	122.38
$IB = 0.63 + 0.25X_A - 0.10X_B + 0.19X_C - 0.093X_AX_B - 0.078X_AX_C - 0.22X_BX_C + 0.16X_A^2$	0.9890	0.9084	0.9749	30.296	0.044
$TS = 21.03 - 3.77X_A - 3.69X_C + 3.40X_AX_C + 6.56\ X_BX_C + 2.18X_B^2 + 4.26X_C^2$	0.9808	0.8958	0.9562	21.680	1.23
$WA = 27.90 - 5.71X_A - 1.50X_B - 6.33X_C + 3.11X_AX_B + 2.32X_AX_C + 6.06X_BX_C + 2.56X_C^2$	0.9856	0.9572	0.9770	24.296	1.33

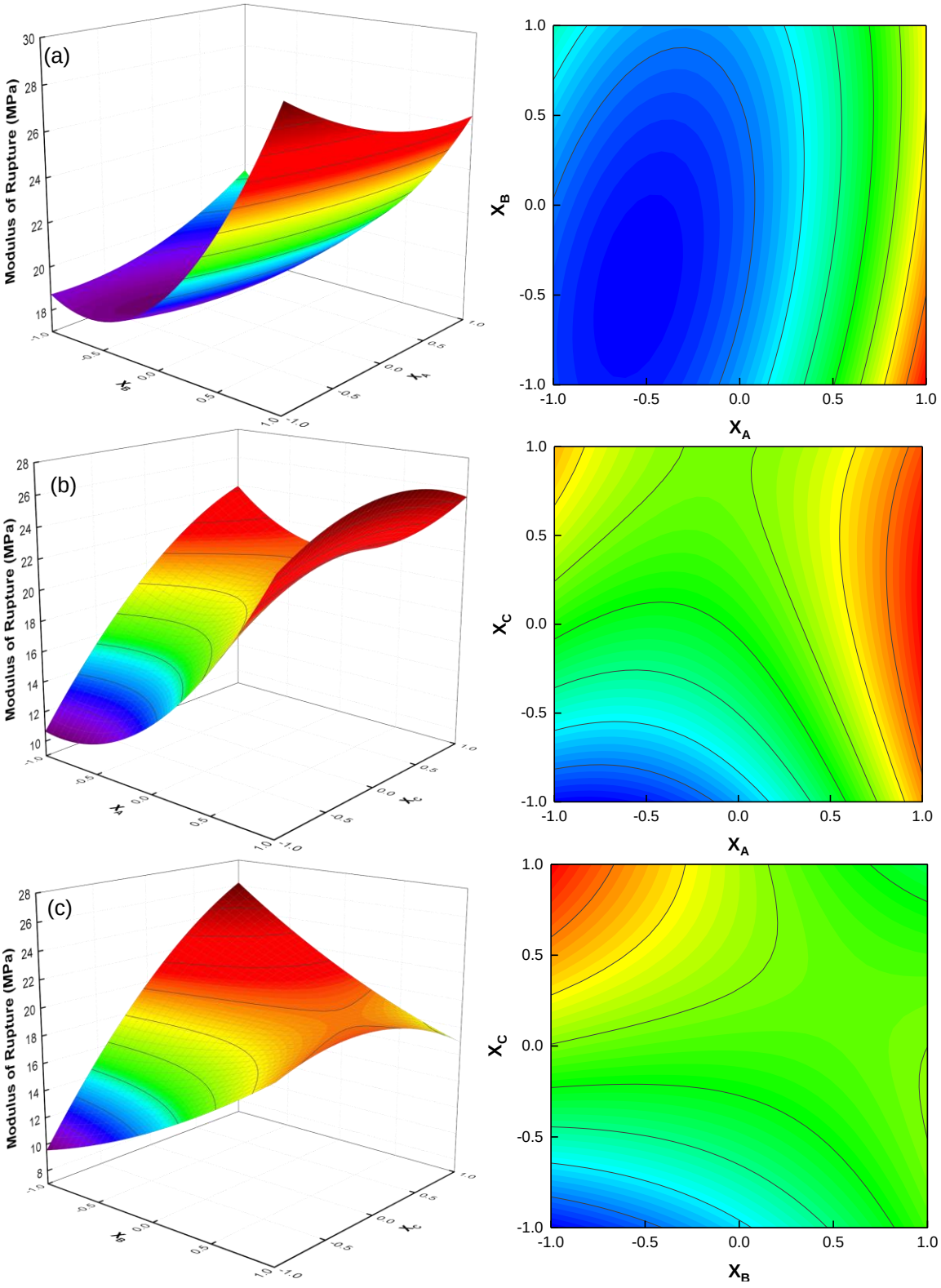

Fig. 1. Response surface plots for MOR as a function of: (a) X_A *vs.* X_B, (b) X_A *vs.* X_C, and (c) X_B *vs*. X_C

A series of estimates yielded five quadratic models associating the mechanical properties to the preparation conditions. These included X_A, X_B, and X_C (Table 3). The models fit well, and all R^2 values were higher than 0.98. All predicted R^2 values agreed with the adjusted R^2 values. Values of adequate precision greater than 4 are desirable (Muthukumar *et al.* 2003). The effects of MOR, MOE, and IB on the mechanical properties and dimensional stability (TS and WA) were investigated more deeply in later sections.

Mechanical Properties

To further analyze the effects of parameters X_A, X_B, and X_C on the mechanical properties of ECS/HML composites, the response surfaces were plotted as three-dimensional (3D) plots. From the generated data obtained from the same test, the MOR and MOE were analyzed together. The fitted models for MOR and MOE yielded R^2 values of 0.9918 and 0.9827, respectively. Table 2 shows that the variables X_A and X_C significantly affected the MOR and MOE while variable X_B was insignificant.

Figures 1a to 1c show the effects of 3D response surfaces of X_A, X_B, and X_C on MOR according to the quadratic mathematical model. At a constant enzymatic pretreatment time (Fig. 1a), the MOR values significantly increased as the mass concentration of laccase-vanillin increased. At a constant mass concentration of laccase-vanillin (1) (Fig. 1b), changes in the trends of MOR were divided into two stages. First, the modified lignosulfonate dosage (X_C) ranged from -1 to 0. As the X_C increased, the MOR value increased, indicating that the crosslinking of the modified lignosulfonate with PEI improved the mechanical strength. Therefore, lignin cross-linked with PEI could be used as a corn panel adhesive. Second, the X_C ranged from 0 to 1.

The MOR values decreased as the modified lignosulfonate dosage increased, suggesting that high amounts of HML could deteriorate the mechanical performance of the ECS/HML composites. The negative value of X_B meant that the decreased enzymatic pre-treatment time increased the MOR values (Fig. 1c). Therefore, excess lignin-based binder can be cured before the final formation of ECS/HML composites. The high amounts of cured lignin-based binder made the samples fragile, which led to the mechanical damage. The same influencing trend was investigated for the MOE and the same explanations of MOR were valid for MOE (Figs. 2a to 2c). The maximum MOR and MOE values of the ECS/HML composites determined at a constant enzymatic pretreatment time of 120 min were 29.18 MPa and 3.148 GPa, respectively.

The response surface plots for the IB are shown in Figs. 3a to 3c. The IB represented the strength of the bonding between the particles and should be considered to ensure that the panels do not delaminate during post-processing. The fitted model for IB yielded an R^2 value of 0.9890. Thus, all single factors and interactions between the mass concentration of laccase-vanillin and other variables (X_AX_B, X_AX_C) were significant for the IB (Table 2). The effects of all variables on IB depicted similar trends. The internal bonding strength generally increased with X_A with X_B and with the enzymatic pretreatment time (X_A). However, Fig. 3 shows that IB was significantly affected by X_A and X_C but moderately affected by time (X_B) in the ECS/HML composites. This suggested that the lignin of corn stalk particles melted well at selected enzymatic pretreated concentrations and selected times, forming strong interparticle bonds at lignin and cellulosic surface areas (Back 1987). Hence, the mechanical properties of ECS/HML composites decreased in the presence of excess amounts of HML. Thus, increased modified lignosulfonate dosage and enzymatic concentration of laccase-vanillin improved the mechanical properties of ECS/HML composites below 15 wt% HML.

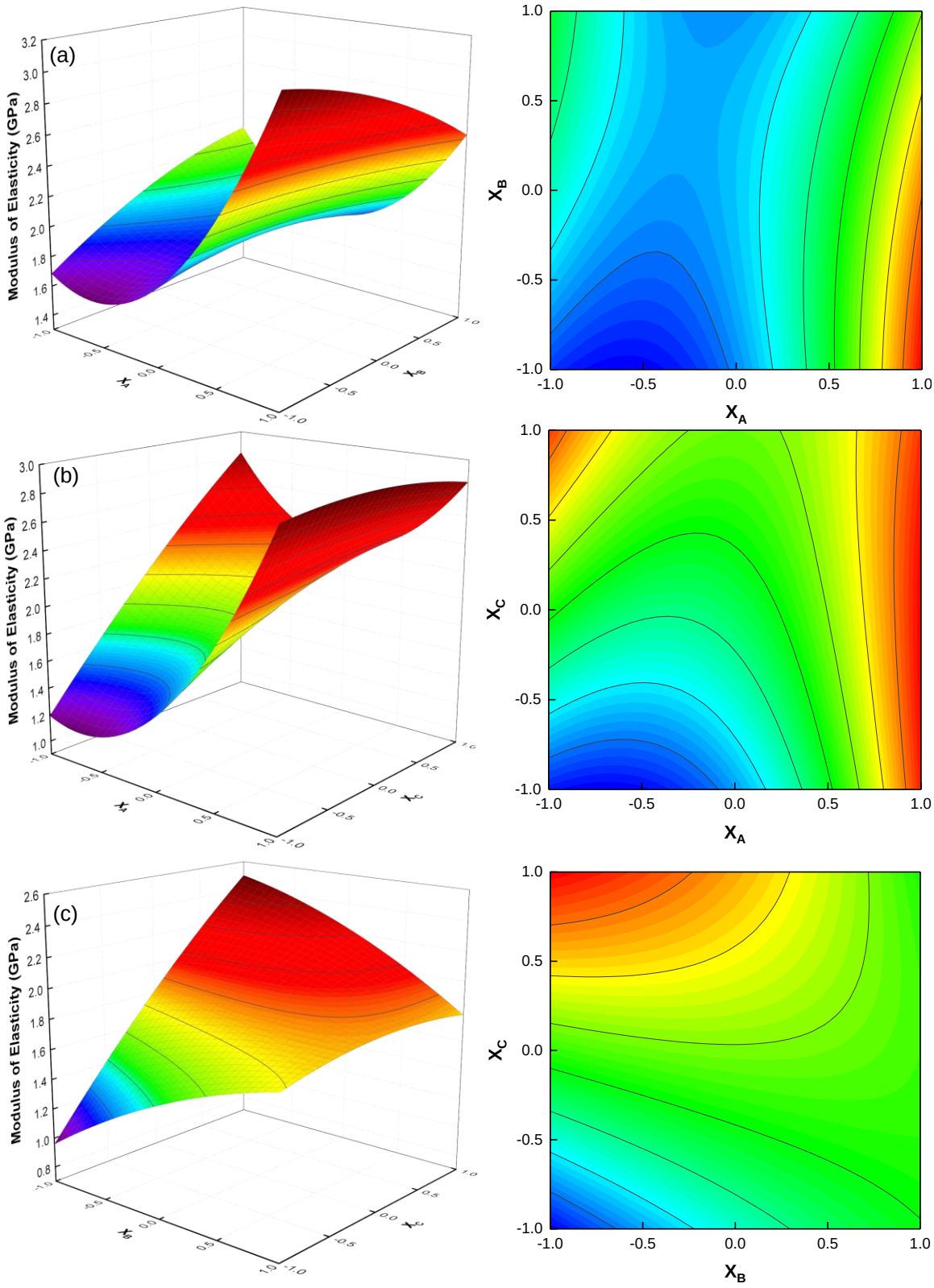

Fig. 2. Response surface plots for the MOE as a function of: (a) X_A *vs.* X_B, (b) X_A *vs.* X_C, and (c) X_B *vs.* X_C

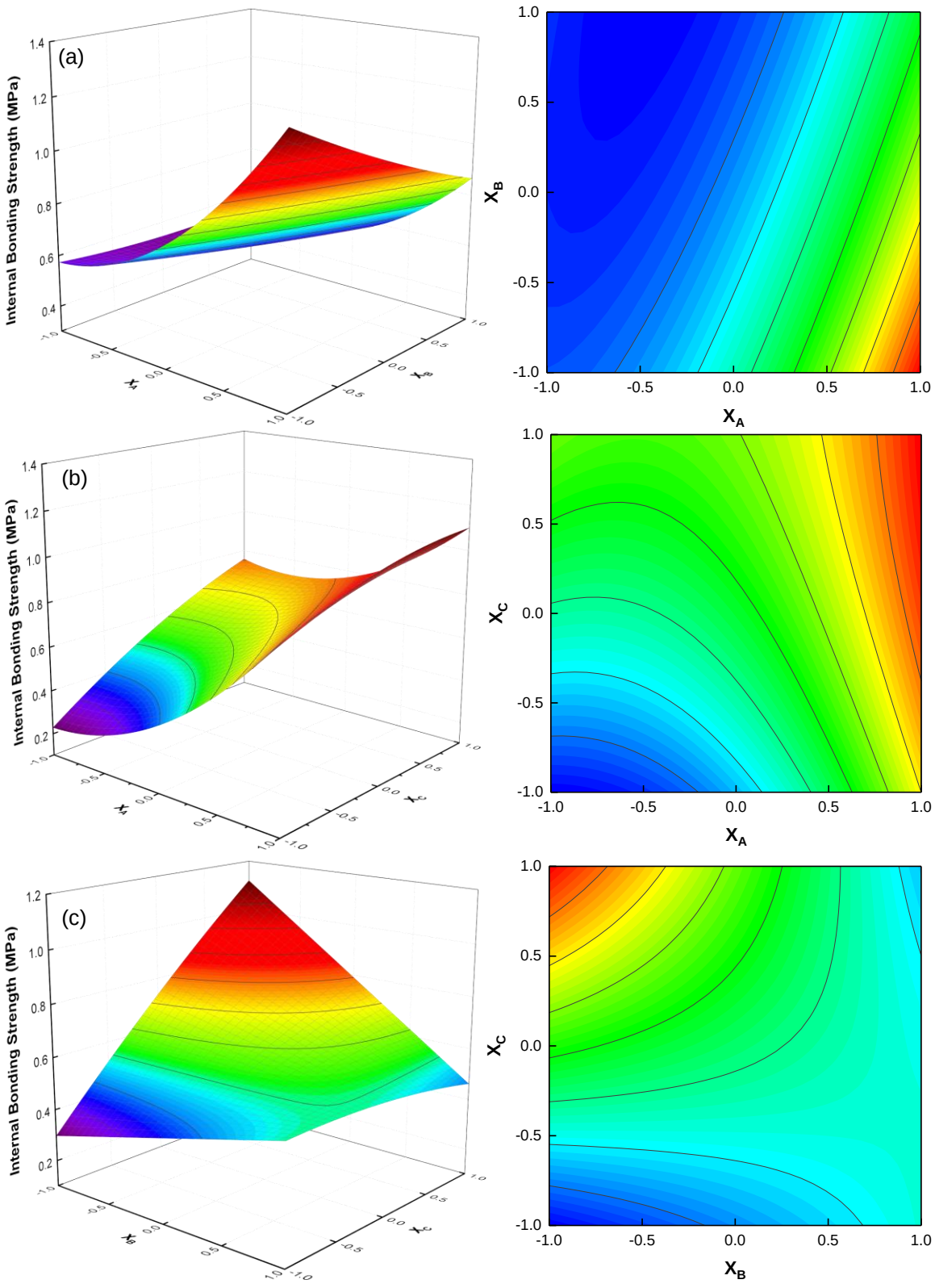

Fig. 3. Response surface plots for IB as a function of: (a) X_A *vs.* X_B, (b) X_A *vs.* X_C, and (c) X_B *vs.* X_C

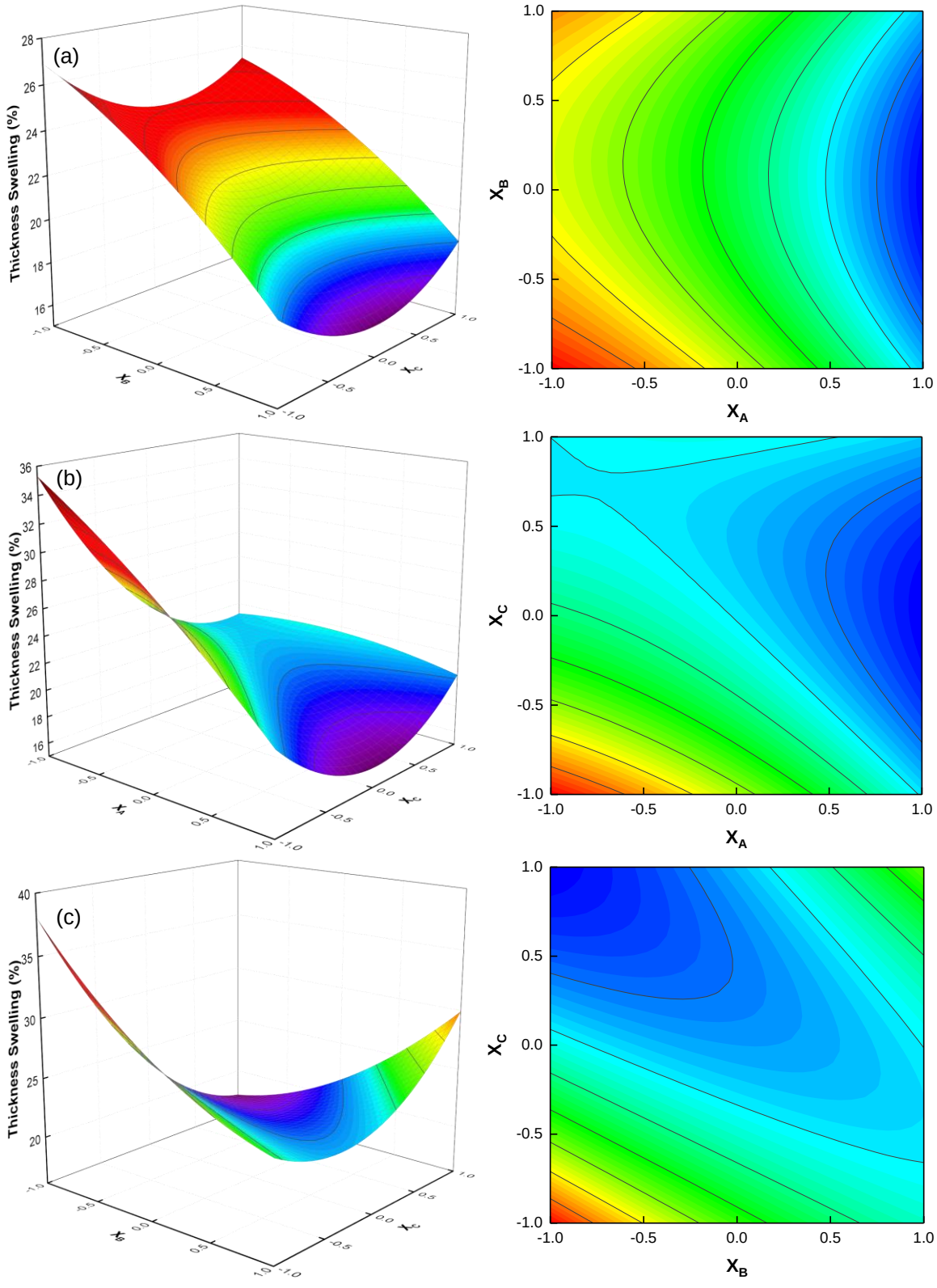

Fig. 4. Response surface plots for TS as a function of: (a) X_A *vs.* X_B, (b) X_A *vs.* X_C, and (c) X_B *vs.* X_C

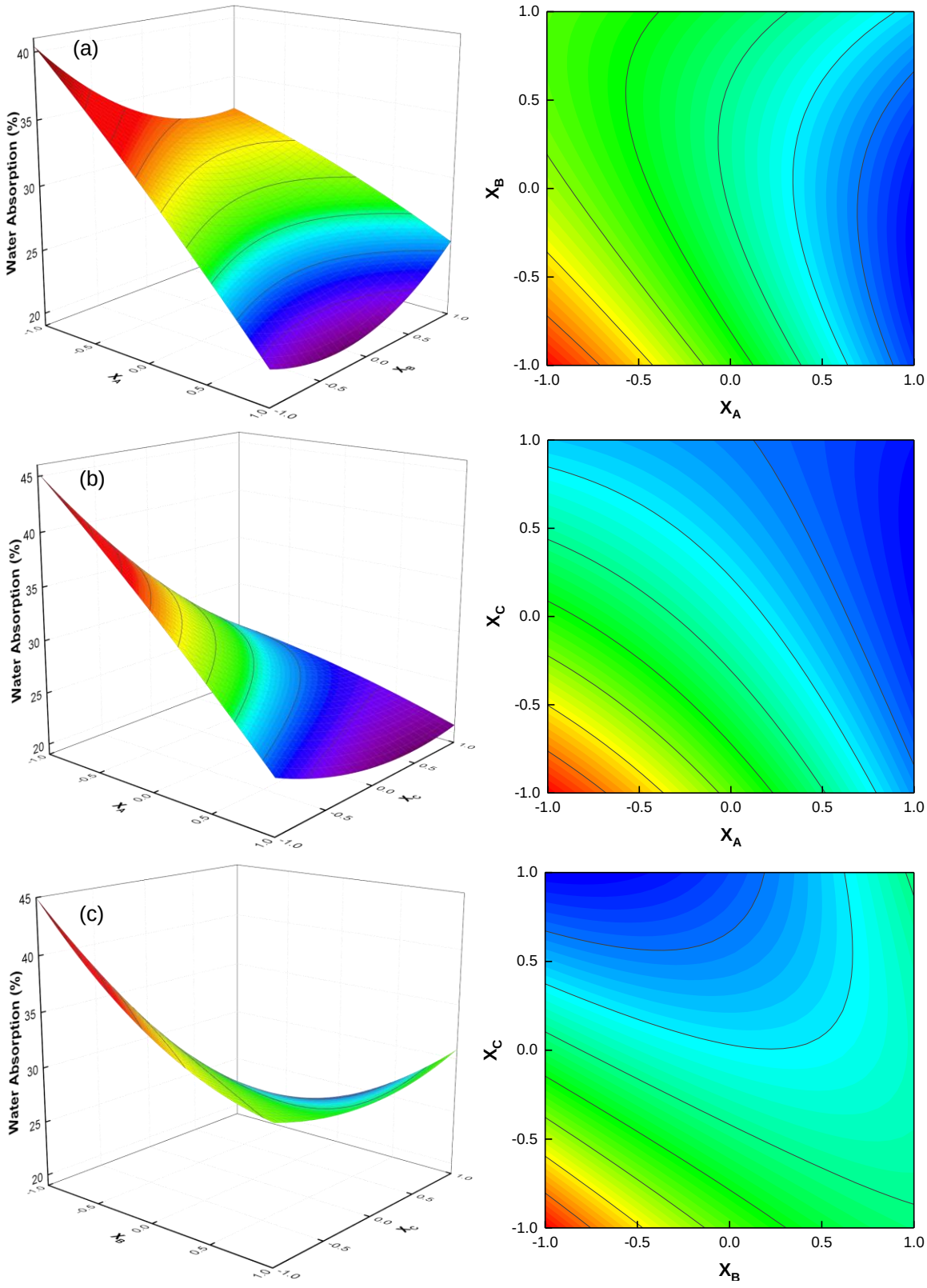

Fig. 5. Response surface plots for WA as a function of: (a) X_A *vs.* X_B, (b) X_A *vs.* X_C, and (c) X_B *vs.* X_C

Dimensional Stability

The TS and WA were determined to be the physical properties associated with the dimensional stability of the ECS/HML composites. The TS and WA were measured under different preparation variables. The fitted models for TS and WA yielded R^2 values of 0.9808 and 0.9856, respectively. The added modified lignosulfonate sufficiently improved the TS and WA performances of the ECS/HML composites when compared to the control panels (Table 1). The correlations between the preparation conditions and TS are shown in Figs. 4a to 4c.

Table 2 indicates that both variables X_A and X_C significantly affected the TS while X_B was insignificant. However, interactions between X_A and X_B did not impact the TS while X_AX_C and X_BX_C were significant. Figures 4a to 4c overall indicated the response surface plots of different combined experimental parameters. The TS scores of panels reduced as X_A increased at a constant enzymatic pretreatment time (X_B), suggesting that X_A positively affected the dimensional stability.

Table 2 also shows the correlations between the preparation parameters and the WA behavior of the panels. Interestingly, all variables and interactions between each other were significant for WA. In contrast, although the TS did not significantly improve as the enzymatic pretreatment time increased, the WA noticeably increased at high mass concentrations of laccase-vanillin and elevated modified lignosulfonate dosage at relatively shorter enzymatic pretreatment times (Figs. 5a to 5c). The reason for this has to do with the chemical modification of the particle cell wall and the relief of residual stresses (Ali *et al*. 2015). Additionally, the addition of HML compacted the board surface by suppressing void spaces, and flowing modified lignin to fill the spaces with covalent interparticle bonds (Back 1987). However, prolonged enzymatic pretreatment time increased the OH content of corn stalk particle surfaces, facilitating water flow in void spaces, and inducing higher WA values of ECS/HML composites.

Optimization of the Preparation Conditions of the ECS/HML Composites

The goal was to figure out the optimal preparation conditions that minimized the TS and the WA without significantly compromising the mechanical properties. The predicted experimental conditions with the highest desirabilities were selected for verification. Under these conditions, desirability achieved 0.976, and the optimum values of manufacturing factors and their responses are given (Table 4).

Table 4. The Optimum Solution Suggested by Design Expert Software

Optimum Condition			Predicted Data					Experimental Data				
A	B	C	MOR (MPa)	MOE (GPa)	IB (MPa)	TS 24 h (%)	WA 24 h (%)	MOR (MPa)	MOE (GPa)	IB (MPa)	TS 24 h (%)	WA 24 h (%)
1	-0.99	0	29.15	3.15	1.26	18.63	21.71	18.4 (3.9)	2.79 (4.3)	1.15 (5.4)	20.1 (2.9)	26.12 (7.4)

A = mass concentration of laccase-vanillin (g/L), B = enzymatic pretreated time (min), and C = modified lignosulfonate dosage (%)

The predicted responses and experimental test results of the ECS/HML composites were compared with indicated deviations less than 10%: 3.4% for MOR, 6.0% for MOE, 4.6% for IB, 3.8% for TS, and 9.2% for WA. The best values were obtained at high mass

concentrations of laccase-vanillin, short enzymatic pretreatment times, and appropriate modified lignosulfonate dosages, which fully met GB/T 4897 (2015). The ECS/HML composites showed 47.2% increase in MOR, 112.9% increase in MOE and 155.6% increase in IB compared to the ECS composites without HML binder. Meanwhile the HML binder positively affected he dimensional properties of the ECS/HML Composites, resulting in 25.6% and 34.7% decrease in TS and WA. The two-part binder was more effective than the default lignosulfonate binder, which negatively affected TS and WA according to previous reports (Hu and Guo 2015).

Synthesis and Characterization of the ECS/HML Composites

Hybrid modified lignosulfate was prepared using an oxidation reaction and combination technology through introducing phenolic hydroxyl and amino groups onto an ECS backbone by ether and ester bonds. The FTIR of corn stalk, ECS, ECS/HML composites, HML, and AL are shown in Fig. 6. Comparing the control corn stalk and ECS, the spectra of both corn stalk and ECS had unique patterns with absorption peaks at 1500 cm^{-1} and 1600 cm^{-1}, due to agricultural lignocellulosic by-products (Buta and Galletti 1989). The -OH bond stretching absorption was discovered between 3309 cm^{-1} and 3320 cm^{-1}, and the C-H bond stretching absorption of methylene groups was found between 2844 cm^{-1} to 2925 cm^{-1}. The aromatic ring vibrations of phenylpropane skeleton were noticed at 1600 cm^{-1}, 1513 cm^{-1}, and 1430 cm^{-1}.

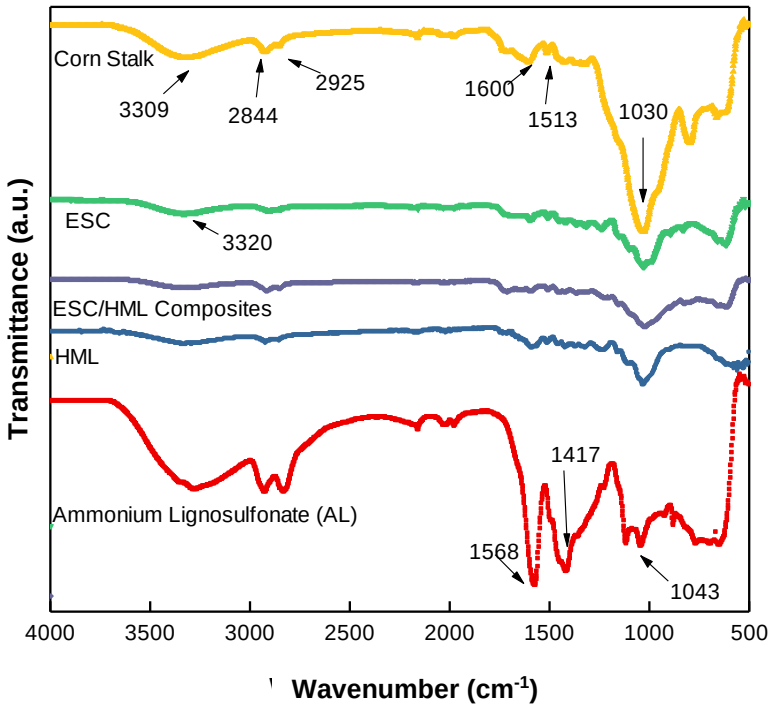

Fig. 6. FTIR spectra of corn stalk, ECS, ECS/HML composites, HML, and AL

The enzymatically treated corn stalks showed lower intensities of syringyl unit (S-bands) from 1328 cm^{-1} and 1030 cm^{-1} due to the enzymatic degradation of lignin. The peaks between 1330 cm^{-1} and 1317 cm^{-1} were assigned to the cellulose part of the particles with improved crystallinity. The carbonyl band, aldehyde, and carboxyl stretching absorptions

of the ECS were weakened at 1714 cm^{-1}, indicating that the enzymatic treatment promoted the esterification reaction of lignin on the surface of particles (Nasir *et al.* 2013). For AL and HML, the methoxyl and sulfonate stretching absorptions of HML were greatly weakened at 1460 cm^{-1} and 1042 cm^{-1} to 1044 cm^{-1}, suggesting a possible cleavage reaction in the presence of H_2O_2. The FTIR spectrum of HML showed new absorption peaks at 1710 cm^{-1} and 1225 cm^{-1} when compared to AL, representing respectively carbonyl stretching and phenolic hydroxyl stretching of HML.

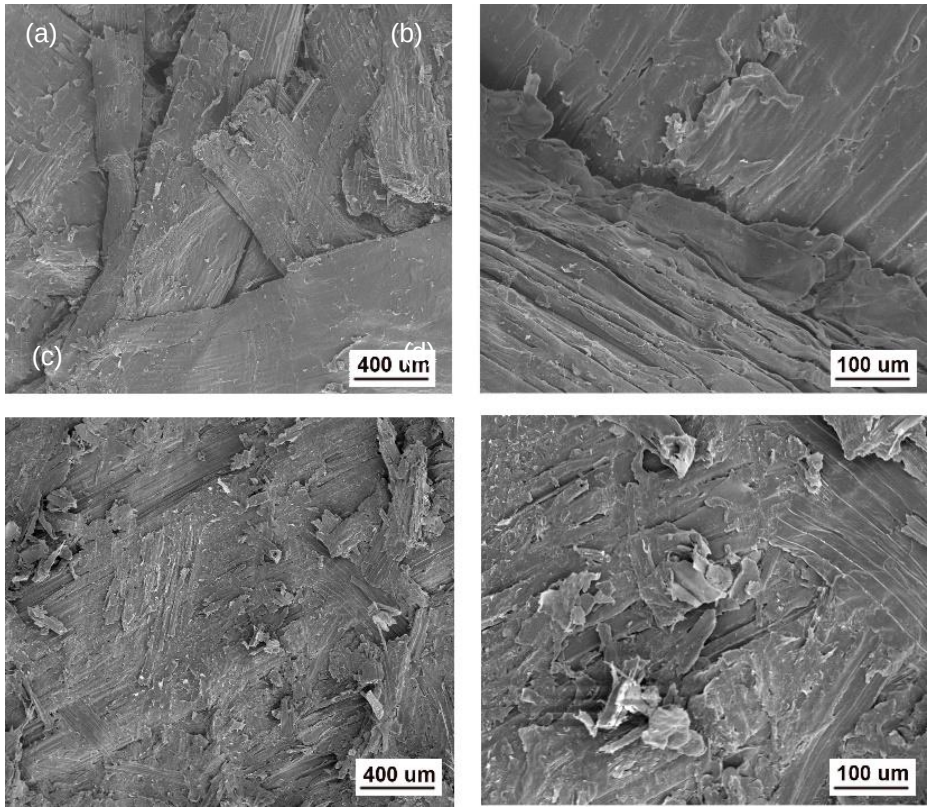

Fig. 7. Micrographs of the ECS panels (a and b) and the ECS/HML composites (c and d)

The absorption bands of phenolic hydroxyl, the -OH stretching of the ECS, and the -NH of HML all were weakened after the fabrication of ECS/HML composites. The latter was formed by covalent bonds or ascribed to electrostatic interactions between the ECS and HML (Ji *et al.* 2017). The differences in the mechanical characteristics of the ECS/HML composites were demonstrated following the IB test shown in Fig. 7. The morphologies of bonding interfaces appeared significantly different. More void spaces were obviously present in the ECS panels when compared to the ECS/HML composites. Moreover, the particle cell walls of the ECS panels almost remained in the original morphologies obtained under hot pressing conditions. Particle debonding clearly occurred in the ECS panels due to poor adhesion, and HML was integrated with the matrix of corn stalk particles in the ECS/HML composites due to good adhesion. Thus, HML looks promising as a binder for corn panels manufacturing.

CONCLUSIONS

1. The preparation conditions of enzymatic pretreatment and modification of lignosulfonate dosage improved the dimensional properties of corn stalk biocomposites.
2. The response surface methodology based on the Box-Behnken method was employed to obtain the optimal conditions. The ECS/HML composites treated under optimal conditions resulted in approximately a 42% reduction of dimensional properties without any significant decline in the mechanical properties when compared to the ECS panels.
3. The statistical analyses demonstrated that individual parameters had more significance than the interactions between these variables. The high mass concentrations of laccase-vanillin for relatively short enzymatic pretreatment times and appropriate modified lignosulfonate dosages reduced residual stresses and improved the dimensional properties. The two-part binder was more effective than the default lignosulfonate binder
4. Composites made from enzymatic pretreated corn stalk and modified lignosulfonate can solve ecological problems by using biomass residues for potential applications.

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