Preparation and Optimization of Chemically Modified Corn Straw/Chitosan/PLA Composite Using RSM

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In this study, an optimized composite was prepared based on chemically modified corn straw, chitosan, and poly(lactic acid) using Response Surface Methodology (RSM). The composite was produced by screw extruding and hot pressing. The Box Behnken Design (BBD) software was used to design the test to optimize the composite composition. The optimum ratio of 3 factors, *e.g.* chemically modified corn straw (0.10 to 0.40 g), chitosan (0.25 to 0.75 g), and poly(lactic acid) (2.00 to 3.00 g) on the response value (bending strength) of the composite was investigated. RSM-BBD provided the optimum combination of composites. The novel composite prepared under the optimized factors was characterized by Fourier transform infrared spectroscopy, mechanical testing, water absorption tests, contact angle tests, and scanning electron microscopy. The results showed that the mechanical strength, *e.g.*, bending strength, impact strength, and tensile strength of chemically modified corn straw based composite were 21.6 MPa, 4.43 kJ/m^2, and 20.0 MPa, respectively, which increased by 23.5%, 13.9%, and 18.7% compared to native corn straw based composite. Improved mechanical strength and hydrophobicity for chemically modified corn straw/chitosan/poly(lactic acid) demonstrated that chemically modified biomass fibers and bio-based degradable polymers have the potential to produce environmentally friendly composites.

DOI: 10.15376/biores.18.4.7943-7962

Keywords: Chemically modified corn straw; Chitosan; Poly(lactic acid); Composite; Box-Behnken design; Response surface methodology

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INTRODUCTION

The industrial production and excessive disposal of traditional petroleum-based plastics has led to global pollution of the natural environment (Claro *et al.* 2016; Beniwal and Toor 2023). It has been reported that more than 330 million tons of plastic are produced worldwide each year (Dixit and Yadav 2019; Mochane *et al.* 2021). By 2050, the amount of plastics produced worldwide is expected to double. Scarcity of non-renewable natural resources and environmental concerns have encouraged the search for alternative degradable polymers (Dehghani *et al.* 2021; Demchenko *et al.* 2022; Fan *et al.* 2023).

Degradable polymers can break down under natural conditions after disposal and have been proposed as a suitable replacement for traditional synthetic polymers (Omerović *et al.* 2021). Great efforts are currently being made to develop novel green composites (Huang *et al.* 2021; Kalita *et al.* 2021; Beniwal and Toor 2023; Elsawy *et al.* 2023). Among many attractive degradable polymer materials, poly(lactic acid) (PLA), poly-β-hydroxybutyrate (PHB), polybutylene succinate (PBS), poly(butylene adipate-co-terephthalate) (PBAT), chitosan (CS), starch, and natural fibers such as crop straw are being studied to synthesize sustainable composites (Fig. 1) (Jamróz *et al.* 2019; Mochane *et al.* 2021; Yanat and Schroën 2021; Kumari *et al.* 2022; Paydayesh *et al.* 2022; Yuan *et al.* 2023). Most bio-based raw materials are biodegradable and non-toxic, which are properties that make them suitable for use in a variety of applications (Liu *et al.* 2020; Wu *et al.* 2022; Ren *et al.* 2023; Setyarini *et al.* 2023).

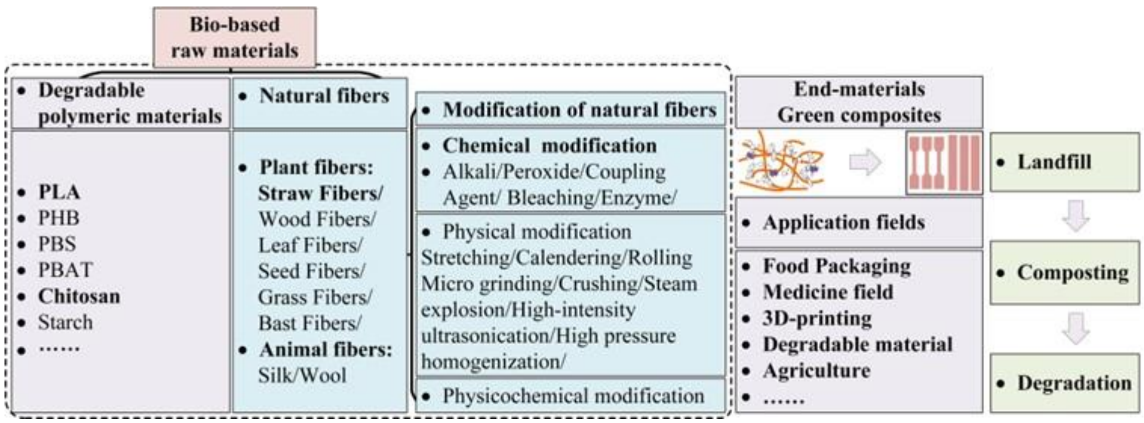


Fig. 1. Typical process for producing novel green composites

Because of PLA's good processability, biodegradability, biocompatibility, thermo-plasticity, good mechanical strength, and reasonable barrier properties, researchers have concentrated their efforts on using PLA in the development of green composites (Kanani *et al.* 2021; Abifarin *et al.* 2022; Eftekhari-Pournigjeh *et al.* 2023). However, PLA's fragility, hydrophilicity, and high cost are the main limitations that have prevented its use in such applications (Claro *et al.* 2016; Mishra *et al.* 2021). To improve toughness, minimize cost, and reduce water uptake, PLA can be blended with other biodegradable ductile polymer materials to reinforce new composites with improved performance (Claro *et al.* 2016; Rizal *et al.* 2021; Ma *et al.* 2022).

Chitosan is an alternative biopolymer with biocompatible, biodegradable, processable, non-toxic, and antimicrobial properties (Claro *et al.* 2016; Chang *et al.* 2021; Jiang *et al.* 2021; Abifarin *et al.* 2022; Li *et al.* 2022). It is obtained from the exoskeleton of shellfish, crustaceans, and insects by deacetylating chitin under alkaline conditions (Jin *et al.* 2020; Lamm *et al.* 2022; Kamaludin *et al.* 2023). It is commercially available and could be considered as an option for recombination with PLA to reduce the cost of novel composites (Claro *et al.* 2016; Kanani *et al.* 2021; Elsawy *et al.* 2023; Kamaludin *et al.* 2023). Previous research on PLA/chitin bio-composites showed that chitosan could be blended with PLA to improve its mechanical properties (Nasution *et al.* 2021; Rizal *et al.* 2021). Claro *et al.* 2016 have obtained PLA-chitosan blends by mixing PLA pellets with either 1 to 2 mm chitosan granules without the addition of plasticizers or additives to synthesize composites with improved thermal and mechanical properties.

Abundant cellulose fiber has been considered as a biopolymer reinforcement to improve the mechanical properties of environmentally friendly composites at comparable cost (Yu *et al.* 2018; Yiga *et al.* 2019; Jin *et al.* 2020; Beniwal and Toor 2023; Islam *et al.* 2023; Song *et al.* 2023). Various natural fibers, including plant fibers (such as straw fibers, wood fibers, leaf fibers, seed fibers, grass fibers, bast fibers, *etc*.) and animal fibers (such as silk and wool) could be used as substitutes in polymers (Mochane *et al.* 2021; Beniwal and Toor 2023). The interfacial interaction between hydrophobic polymers and hydrophilic fibers is known to be very weak from the literature (Song *et al.* 2023). This has an impact on the properties of the resulting cellulose fiber/biopolymer composites. Various pretreatment processes for cellulose fibers, including chemical modification, physical modification and physicochemical modification, have been used to improve the interfacial interaction between the fiber and polymer matrices (Beniwal and Toor 2023; Fan *et al.* 2023; Ren *et al.* 2023). This process, which involves improving the interfacial bonding between fibers and polymer matrices, could improve the mechanical properties of bio-composites (Mochane *et al.* 2021). It has been reported that among the various surface modification processes, chemical modification of the fibers could help remove lignin, impurities, and waxes, improve adhesion, and improve the fiber/matrix interface (Huang *et al.* 2021; Ren *et al.* 2023). Furthermore, according to published results, the modification of straw with silane coupling agents plays a detrimental role in promoting the interfacial interaction between hydrophobic polymers and hydrophilic fibers (Daghigh *et al.* 2018; Sahai and Pardeshi 2019; Bahrami *et al.* 2021; Bahrami and Bagheri 2022).

Corn is considered one of the world's top three food crops, with corn straw production at 1.25 billion tons per year, or 26% of the world's total straw production (FAO Statistical Yearbook). Corn straw (CS) contains 34 to 40% cellulose, 28% hemicellulose, and 7 to 21% lignin (Mochane *et al.* 2021). Due to its availability, biodegradability, biocompatibility, low cost, adequate mechanical strength, and environmental friendliness, corn straw is considered promising for the production of natural fiber green composites. In order to improve the compatibility and interface between the hydrophobic polymer matrix and the hydrophilic straw fiber, the chemical modification of straw has been investigated and reported (Dixit and Yadav 2019). Chemical modification changes the structure, composition and properties of straw, which is expected to enhance the fiber strength and mechanical performance of composite materials (Song *et al.* 2023). Huang *et al.* 2021 investigated the alkali treated straw reinforced geopolymer composites and evaluated the bending strength, water absorption, swelling rate and water absorption of the composite. The results showed that the alkali treated straw had a greater strengthening effect. The bending strength of the alkali-treated straw-reinforced geopolymer composites with 10% fiber content reached 13.6 MPa, which exceeds the superior product requirement (≥10 MPa) specified in the national standard "Cement Bonded Particleboard" (Huang *et al.* 2021). Song *et al.* 2023 modified straw flour with 1 to 7 wt% NaOH solution, 0.5 to 2 wt.% (3-aminopropyl) triethoxysilane solution or NaOH+silane solution synergistic impregnation and pretreated straw filled with poly(3-hydroxybutyrate) (PHB) to produce bio-composites. The best result was obtained with 3 wt% NaOH + 0.5 wt% silane, which increased strength (flexural, tensile, and impact) and modulus (flexural, tensile) by 22 to 40 % and 14 to 23 % respectively, reduced 300 h water absorption by 18 %, reduced water contact angle by 7 to 24°. Alkali treatment removed unstable, amorphous substances on straw flour, resulting in higher mechanical, waterproof nature, and heat resistance of composites (Huang *et al.* 2021; Song *et al.* 2023). Improved performance and a wide range of applications are demonstrated by the resulting bio-composite. Currently, several types of natural fibers were used to reinforce non-biodegradable polymers such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), high-density polyethylene (HDPE), polyurethane (PUR), *etc.* for the production of composite materials (Dixit and Yadav 2019; Mochane *et al.* 2021).

Response Surface Methodology (RSM)-Box-Behnken Design (BBD) is a technique for analyzing the effects of different independent variables to find the optimized state. The suitability of the method for optimizing independent variables with less experimental time has been claimed in many studies (Kandar and Akil 2016; Tharazi *et al.* 2017). For instance, Kandar and Akil (2016) used RSM-BBD to optimize the process parameters of hot press forming to improve the mechanical properties of woven flax/PLA composites. Tharazi *et al.* (2017) optimized the hot pressing parameters on the tensile strength of unidirectional long kenaf fiber reinforced PLA composite by RSM-BBD. The influence of three independent process variables on the impact strength of composites was investigated. In principle, the Box-Behnken design can help reduce the time spent on research and development.

To date, no relevant studies on producing biodegradable materials from corn straw, chitosan, and PLA have been reported. In line with our applications, this paper has used Response Surface Methodology (RSM) and Box-Behnken Design (BBD) to optimize the various independent factors to achieve the best possible output response. This experimental design was chosen in order to reduce the number of experiments, to optimize the process parameters and to obtain the most favorable values (Dixit and Yadav 2019). In this study, RSM-BBD was used to optimize the process variable of chemically modified corn straw/chitosan/PLA based bio-composite. The effect of the independent variables on the bending strength of the composite material and the optimum combination for the composite material were observed. A total of 17 sets of experiments were carried out on the basis of different mass fractions of NaOH modified corn straw, chitosan, and PLA. In addition, the novel composite prepared under the optimized factors was further analyzed and characterized by Fourier transform infrared spectroscopy, mechanical test, water absorption test, contact angle test, and scanning electron microscopy to assess its suitability for the production of environmentally friendly composites.

EXPERIMENTAL

Materials

Corn straw (CS) was sourced from Guangxi Province, China. CS was crushed, oven-dried, and sieved through a 100 mesh screen. First, 10 g of sieved corn straw was exposed to 100 mL of NaOH (10%, w/v%) at room temperature for 24 h. The desired residues for treated CS were washed to neutrality with deionized water, filtered, and dried (80 °C, 12 h).

Poly(lactic acid), size 100 mesh, was purchased from Foshan Zogao Plasticizing Co., LTD, Foshan, Guangdong Province, China. Chitosan (acid soluble), size 100 mesh, was purchased from Guangzhou Fenggrao Chemical Co., LTD, Guangzhou, Guangdong Province, China. The silane coupling agent used in this paper was KH-560 (liquid), which was purchased from Shanyi Plastic Chemical Co., Ltd., Guangdong Province, China.

Preparation of Chemically Modified Corn Straw/Chitosan/Poly(lactic acid) Composites

The composites, based on different proportions of chemically modified corn straw, chitosan, and PLA, were produced by screw extrusion (SJ15, Zhangjiagang Orode Machinery Co., LTD, Jiangsu, China) and hot-pressing (Plate vulcanizing machine, XLB, Shanghai Rubber Factory, Shanghai, China) (Fig. 2). NaOH-modified corn straw was modified with a silane coupling agent (KH-560 liquid solution, 5 wt%) and dried in an oven at 80 °C prior to the preparation of the bio-composite. NaOH-modified corn straw, chitosan, and PLA were then mixed uniformly in a specific ratio recommended by the RSM-BBD software (Table 1).

The mixed materials were fed into a screw extruder and pelletized. Granulated materials were placed in a standard mold and hot pressed (160 °C, 18 min, 10 MPa) to produce the composites. Figure 2 shows the preparation process.

Experimental Design Using RSM-BBD

In this study, BBD was used to determine the optimized conditions for the preparation of chemically modified corn straw/chitosan/PLA-based composites. The percentage of chemically modified corn straw, chitosan, and PLA were chosen as process variables.

The responses obtained from the experiments (the bending strength of the composites) were used to optimize the variables. Listed below (Table 1) are the coded and actual values for the process variables (selected on the basis of single factor experiments) of RSM-BBD. By default, the high levels of the factors are coded as 1 and the low levels are coded as -1. The Design Expert software (version 13) was used to derive the 17 experiments required for this model (Table 2). According to the levels for each variable, there should be 27 experiments (runs), which were reduced to 17 experiments using the Design Expert software.

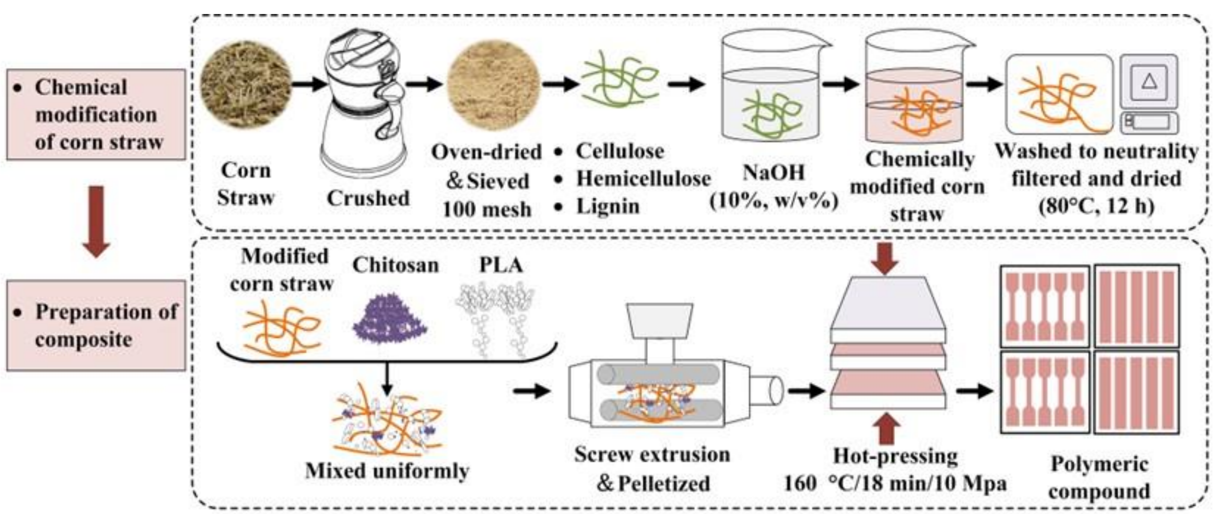


Fig. 2. Process for the preparation of chemically modified corn straw/chitosan/poly(lactic acid) composites

Table 1. Coded Levels and Actual Values for the Process Variables

Process Variables	Coded Levels and Actual Values		
	-1	0	1
A Poly(lactic acid) (g)	2.00	2.50	3.00
B Chitosan (g)	0.25	0.50	0.75
C Chemically Modified Corn Straw (g)	0.10	0.25	0.40

Regression analysis of the experimental data (response values) was carried out to optimize the variables and determine the coefficients of the mathematical equation. The following is a representation of the polynomial regression model:

$$R = \gamma_0 + \sum_{n=1}^{k} \gamma_a \, x_a + \sum_{a=1}^{k} \gamma_{aa} x_a^2 + \sum_{1<a<b}^{k} \gamma_{ab} x_a \, x_b + \varepsilon \tag{1}$$

In Eq. 1, R is the response (bending strength of the composite material), and ε indicates the random error in this study. The process factors were indicated by χ_α. The parameters γ_0, γ_a, γ_{aa}, and γ_{ab} represent the offset, linear, quadratic and interaction coefficients, respectively.

Compositional Analysis of Native and Chemically Modified Corn Straw

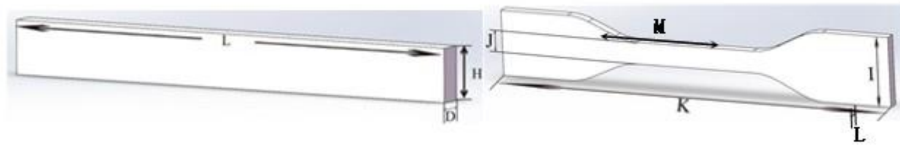
The composition of native and chemically modified corn straw was measured using the National Renewable Energy Laboratory's NREL method (Sluiter *et al.* 2008). The compositional changes of cellulose, hemicellulose, acid-soluble lignin, and acid-insoluble lignin for corn straw before and after chemical treatment were determined in this study.

Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared spectroscopy (FTIR) analysis for composites was performed using a Fourier transform infrared spectrometer (IS50, Thermo Fisher Scientific, USA). Sample powder (0.001 g) was dried in an oven at 80 °C for 8 h for FTIR analysis. The samples were tested over the wavenumber range from 500 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans in attenuated total reflection mode (Dehghani *et al.* 2021).

Mechanical Properties of Composites

Mechanical properties such as bending strength, tensile strength and impact strength were tested. The bending strength for composites was determined using a universal testing machine referring to the ASTM D790 (2017) standard (KRWDW-100E, Jinan Kerui Testing Machine Manufacturing Co. LTD, Shandong, China). The dimensions of the composite specimens prepared for the bending strength test were 127 mm × 12.7 mm × 3.2 mm (Fig. 3a). To obtain the average value, the strain rate was set at 0.01 mm/min and repeated 3 times. The impact strength of the composites was measured using an impact tester in accordance with ISO 180 (2019) standard (Digital Display Impact Tester ST-5.5D, Xiamen Ester Instrument Co., Ltd., Fujian, China). The dimensions of the composite specimens prepared for impact testing were 80 mm × 10 mm × 4 mm (Fig. 3a). The tensile strength of composites was determined using a PC auto tensile tester according to the ASTM D412 (2021) standard (DLS-07, Jinan Sum spring Experimental Instrument Co., Ltd., Shandong, China). The dimensions of the dumbbell-shaped composite specimens prepared for the tensile test were 115 mm × 6 mm × 3 mm, gage length 25 mm (Fig. 3b).



(a) (b)

Fig. 3. Dimensions of composite specimens prepared for mechanical testing
(a: bending strength, L=127 mm, H=12.7 mm, D=3.2 mm; a: impact strength, L=80 mm, H=10 mm, D=4 mm; b: tensile strength, K=115 mm, J=6 mm, L=3mm, M=25 mm, I=18 mm)

Analysis of Water Absorption

The water absorption properties of chitosan/PLA, native corn straw/chitosan/PLA composites and chemically modified corn straw/chitosan/PLA composites were determined according to ASTM D570 (2022). Samples with dimensions of 10 mm × 10 mm were immersed in distilled water for a period of 24 hours. The water absorption results for the samples were calculated using the following formula, based on the change in weight before and after immersion in water.

$$\text{Water absorption result (\%)} = \frac{\text{Final weight(g)} - \text{Initial weight (g)}}{\text{Initial weight (g)}} \times 100 \qquad (2)$$

Contact Angle Analysis

The contact angle for chitosan/PLA, native corn straw/chitosan/PLA based composites, and chemically modified corn straw/chitosan/PLA based composites were investigated using a drop shape analyzer to detect the hydrophobic property of the samples (JY-PHa Contact Angle tester, China). In order to obtain the average value, the tests were repeated 5 times at room temperature (Nasution *et al.* 2021).

Scanning Electron Microscopy (SEM)

A field emission scanning electron microscope was used to determine the fractured surface morphology of chitosan/PLA, native corn straw/chitosan/PLA-based composites and chemically modified corn straw/chitosan/PLA based composites (SU5000, Hitachi High Technology Co, Japan). An ion sputtering device was used to sputter gold onto the fractured surface of the samples for 1 minute (Claro *et al.* 2016)

RESULTS AND DISCUSSION

RSM and ANOVA Analysis

RSM-BBD model suitability check

Table 2 shows the predicted values and the actual values after the execution of the experiments, as provided by RSM-BBD. Actual values represent response data obtained from 17 sets of test runs. The predicted values were derived from the RSM in conjunction with the BDD model. ANOVA analysis was used to analyze the results obtained.

The relationship between actual and predicted values of the mathematical mode is shown in Fig. 4. All variable data points in the graph below are spread around the diagonal line. This result suggests that the mathematical model provided by the design expert software was appropriate and reliable (Dixit and Yadav 2019).

Table 2. Predicted Values and Actual Values of the Bending Strength after Performing the Tests Provided by RSM-BBD

Actual Variable Values provided by RSM-BBD					Predicted Values and Actual Values of the Bending Strength (Response)	
Standard Order	Run	Poly(lactic acid) (g)	Chitosan (g)	Chemically Modified Corn Straw (g)	Actual Value (MPa)	Predicted Value (MPa)
1	R04	2	0.25	0.25	12.01	12.26
2	R03	3	0.25	0.25	13.91	14.66
3	R13	2	0.75	0.25	10.53	9.78
4	R16	3	0.75	0.25	16.04	15.79
5	R15	2	0.5	0.1	18.92	19.65
6	R06	3	0.5	0.1	17.75	17.98
7	R12	2	0.5	0.4	10.58	10.35
8	R08	3	0.5	0.4	21.16	20.43
9	R05	2.5	0.25	0.1	12.11	11.13
10	R10	2.5	0.75	0.1	17.73	17.75
11	R02	2.5	0.25	0.4	15.02	15.00
12	R09	2.5	0.75	0.4	6.05	7.03
13	R11	2.5	0.5	0.25	17.67	17.22
14	R17	2.5	0.5	0.25	18.52	17.22
15	R01	2.5	0.5	0.25	17.26	17.22
16	R07	2.5	0.5	0.25	13.66	17.22
17	R14	2.5	0.5	0.25	18.99	17.22

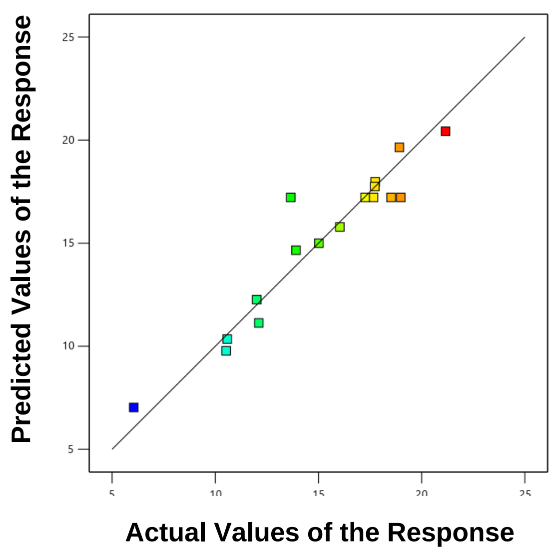


Fig. 4. Relationship between actual values and prediction values of the mathematical model

Effect of process variables on the response

The RSM-BBD model suggests the following polynomial statistical equation (Eq. 3) that optimizes the process parameters for the bending strength of the bio composite.

$$R = 17.22 + 2.10A - 0.3375B - 1.71C + 0.9025AB + 2.94AC - 3.65BC + 0.1387A^2 - 4.24B^2 - 0.2562C^2 \tag{3}$$

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. The linear terms of the RSM-BBD model are represented by the parameters *A*, *B*, and *C*. The products *AB*, *BC*, and *AC* show the interacting terms. The squared quantities A^2, B^2, and C^2 represent the quadratic terms of the RSM-BBD model. The coded equation was useful for identifying the relative impact of the factors by comparing the factor coefficients.

Table 3. ANOVA Analysis for the Bending Strength of Bio-composites Using RSM-BBD

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	227.31	9	25.26	8.02	0.0060	significant
A Poly(lactic acid) (g)	35.36	1	35.36	11.23	0.0122	
B Chitosan (g)	0.9112	1	0.9112	0.2894	0.6073	
C Chemically Modified Corn Straw (g)	23.46	1	23.46	7.45	0.0294	
AB	3.26	1	3.26	1.03	0.3429	
AC	34.52	1	34.52	10.96	0.0129	
BC	53.22	1	53.22	16.90	0.0045	
A^2	0.0811	1	0.0811	0.0257	0.8771	
B^2	75.56	1	75.56	23.99	0.0018	
C^2	0.2765	1	0.2765	0.0878	0.7756	
Residual	22.04	7	3.15			
Lack of Fit	4.34	3	1.45	0.3272	0.8072	not significant
Pure Error	17.70	4	4.43			
Cor Total	249.35	16				
Std. Dev.	1.77		R^2	0.9116		
Mean	15.17		Adjusted R^2	0.7979		
C.V. %	11.70		Predicted R^2	0.6104		
			Adeq Precision	9.8454		

The F-value of the model was 8.02, indicating that the model was significant (Table 3). There was only a 0.60% chance that an F-value this large could occur due to noise. P-values less than 0.0500 were an indication that the model terms were significant. In this case, *A*, *C*, *AC*, *BC*, and B^2 were significant terms in the model. Values greater than 0.1000 indicate that the terms in the model were not significant. The most influential factor in the response was the addition of poly(lactic acid) (F = 11.23), followed by chemically modified corn straw (F = 7.45). The lack of fit F-value of 0.33 indicated that the lack of fit was not significant relative to the pure error. There was an 80.72% chance that a lack of fit F-value of this magnitude could occur due to noise. The value of the regression correlation coefficient R^2 was 0.91. The predicted R^2 was in reasonable agreement with the adjusted R^2; *i.e.* the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 9.845 indicated an adequate signal. In summary, this model can be used to navigate the design space.

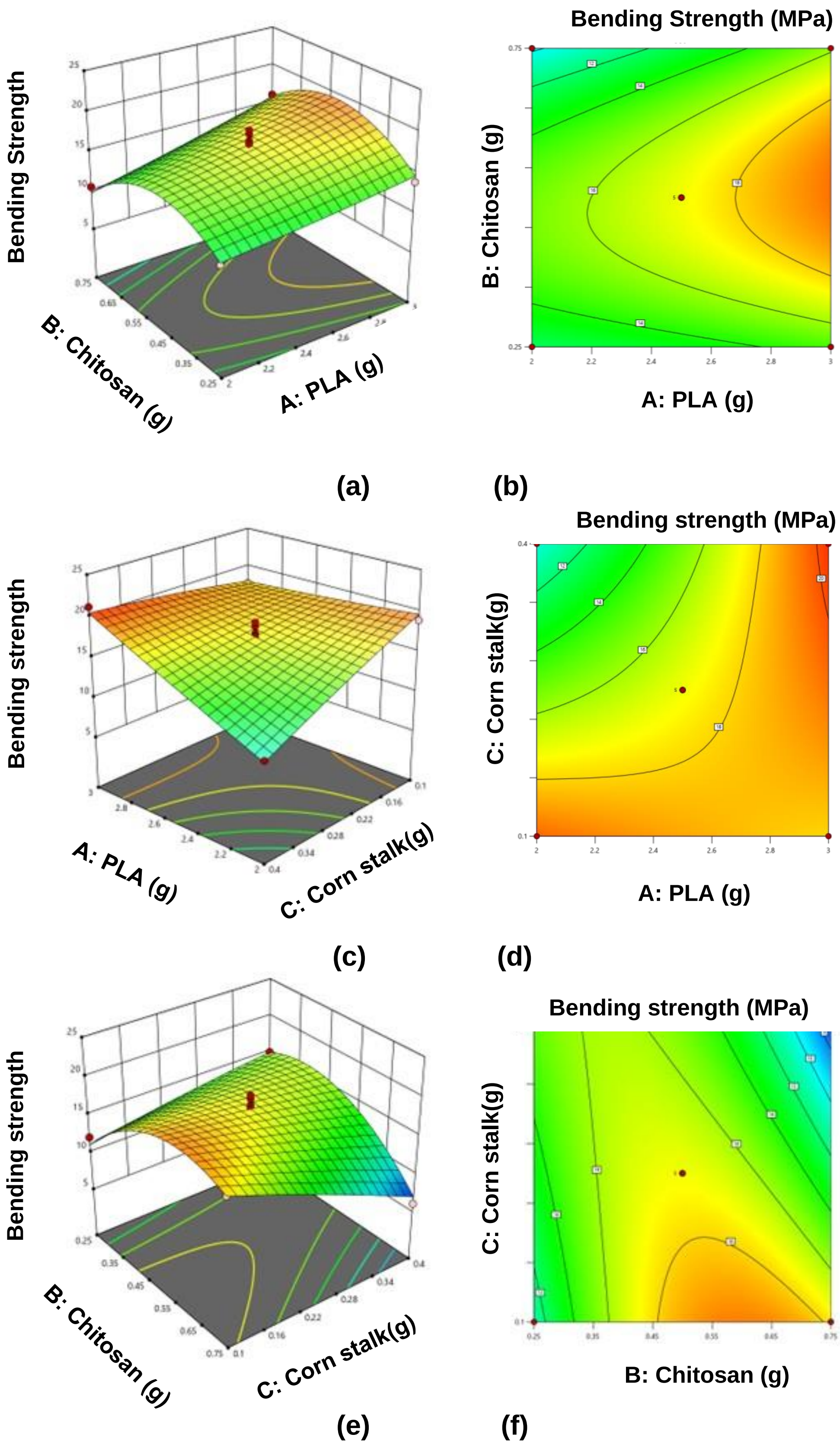


Fig. 5. Contour plots and 3D surface for bending strength of composites using RSM-BBD

Response surface plots for the bending strength of composites are shown in Fig. 5. The bending strength of the composite was significantly affected by the addition of poly(lactic acid). The bending strength of the composites increased with increasing PLA content (from 2.00 to 3.00 g) when other process factors were held constant. The bending strength of the composites decreased as the amount of NaOH modified corn straw increased (from 0.10 to 0.40 g). The addition of chemically modified corn straw to the composite affected the tensile strength value within a certain range (Figs. 5c to 5f). Similar trends have been observed previously (Qiao *et al.* 2022). There was an insignificant effect (P = 0.6073) of chitosan (from 0.25 to 0.75 g) on the bending strength of the composite.

It can be concluded that the use of poly(lactic acid) and chemically modified corn straw significantly affected the mechanical strength of the composite, as confirmed by the modelling results above. This result ensures the optimization of composite components for the synthesis of novel composites with better mechanical properties.

Optimization of the RSM-BBD statistical model

The optimized concentrations of chemically modified corn straw, chitosan, and PLA supplied by RSM-BBD were 0.40 g, 0.41 g and 3.00 g respectively, giving a bending strength of 20.99 MPa. Small percentages of error were found for the response value, demonstrating the reliability of the RSM-BBD statistical model to obtain the desired bending strength under optimized conditions for the variables (Dixit and Yadav 2019).

Compositional Analysis of Native and Chemically Modified Corn Straw

The analyses for the composition of the native corn straw and the chemically modified corn straw are shown in Fig 6.

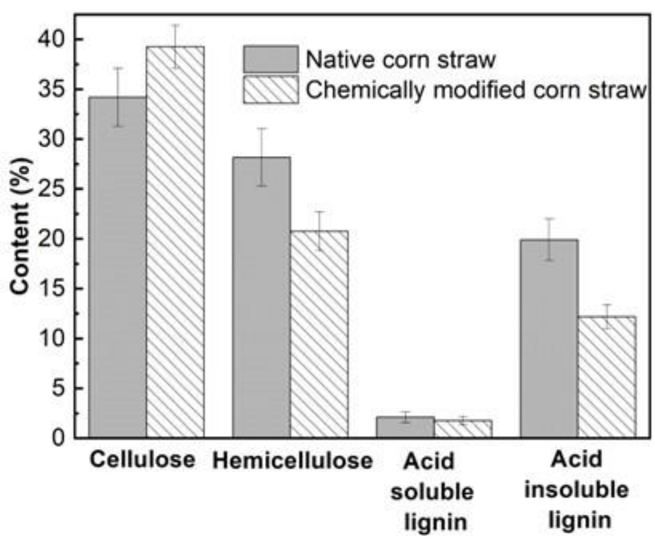


Fig. 6. Compositional analysis result of native and chemically modified corn straw

The hemicellulose content (dry basis) decreased from 28.17% to 20.77% after chemical modification. Acid soluble and insoluble lignin content decreased from 2.11% to 1.78% and 19.9% to 12.17% respectively. One possible explanation was that the chemical modification removed a certain amount of the lignin, hemicellulose and pectin found in the S2 layer of the secondary cell wall of the fibers; this could reduce the obstacles to formation of strong adhesive bonds (Dixit and Yadav 2019; Huang *et al.* 2021; Mochane *et al.* 2021).

The results shown in Fig. 6 also express the increase in the desirable cellulose content of the corn straw after chemical modification. The cellulose content of the corn straw was increased from 34.21% to 39.26% after the NaOH modification. A possible explanation for these results was that, due to the weak endwise peeling and alkaline hydrolysis-induced by NaOH, the 10% (w/v%) NaOH was primarily a swelling agent for the cellulose bundles (Browning 1963; Sixta 2006), especially in the amorphous region, and then in the crystalline region, which can be easily and temporarily added to the cellulose chains, forming an additional compound (alkali cellulose, which was industrially prepared using 17.5 to 18% NaOH). After the chemical modification of natural fibers, the nature of the fibers was changed to improve their compatibility with polymers for the reinforcement of bio composites (Song *et al.* 2023). Alkali modification can leave the fiber cleaner and rougher than before, which helps to increase the contact area between different materials and was beneficial for the subsequent composite preparation process. Previous studies have reported similar results (Dixit and Yadav 2019).

Characterization of the Optimized Chemically Modified Corn Straw/ Chitosan/PLA Composites

FTIR

Fourier transform infrared spectroscopy for chitosan/PLA composites, native corn straw/chitosan/PLA composites and chemically modified corn straw/chitosan/PLA composites are shown in Fig. 7. The characteristic peak at 3357 cm^{-1} corresponds to the vibration of -OH groups found in chitosan, cellulose, hemicellulose and lignin in corn straw. The peaks around 2933 cm^{-1} and 1358 to 1449 cm^{-1} represented the stretching and bending vibrations of C-H, which were found in the main chain of PLA, chitosan and fiber components. The absorption peaks at 1080 cm^{-1}, 1178 cm^{-1} and 1747 cm^{-1} represent the Al-O groups, stretching vibrations of C-O and C=O groups, respectively, found in PLA, chitosan and fiber components for all samples. The absorption peak around 1000 to 1270 cm^{-1} represents the aromatic oxide. This confirms the presence of lignin in natural fiber-based bio-composites.

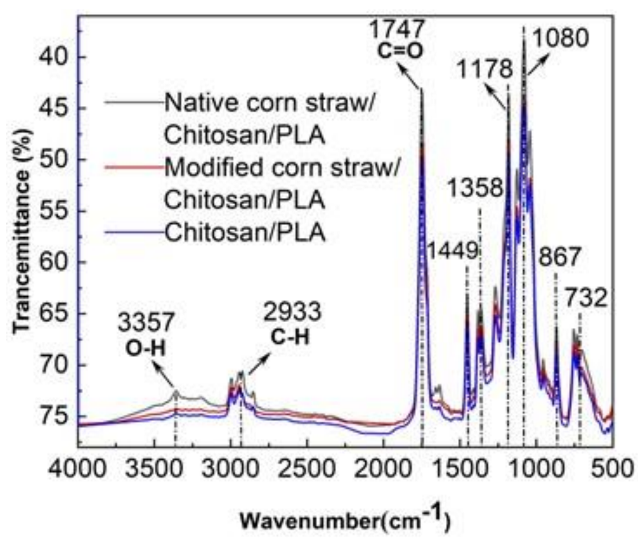


Fig. 7. FTIR (Fourier transform infrared spectroscopy) analysis for composites

Differences in the characteristic peak of -OH groups for native corn straw based composite and chemically modified corn straw based composite were observed in the figure above. An apparent reduction in the proportional content of hydroxyl groups (-OH) of the natural fibers could be attributed to conversion of OH groups to alkoxides. The C=O absorption intensity and the characteristic region of lignin for the NaOH modified corn straw composite were lower than for the native corn straw composite. The difference was probably attributable to the reduction in fiber (lignin and hemicellulose) contained in the corn straw that leached out when treated with NaOH. This result could correspond to the compositional analysis result of native and chemically modified corn straw in Fig. 6. This result has been linked to the ability of the chemically modified corn straw in a polymer matrix to remove some of the lignocellulosic components, increase the contact area, improve the fiber/matrix interface and adhesion. Researchers have observed similar results in the literature that they have published (Dixit and Yadav 2019; Feng *et al.* 2020).

Contact angle analysis

The contact angle test results for composites are shown in Fig. 8. The contact angle values for chitosan/PLA, native corn straw based composites and chemically modified corn straw based composites were 87°, 76°, and 82° respectively. Compared to native corn straw composites, the contact angle for chemically modified corn straw composites was higher (increased by 6°). The contact angle results indicate the surface hydrophilicity of the bio composite. In general, the surface tension between the bio-composite sample and water is influenced by surface roughness and hydrophilic groups. The loading of the straw has a significant negative effect on the hydrophobicity of the straw reinforced composites (Qiao *et al.* 2022). Alkali modified corn straw-based composites showed improved hydrophobicity and waterproofing properties after NaOH affected the surface structure of the natural fibers. This result could be due to the increased interfacial interaction of the polymer with the surface modified straw and the improved physicochemical properties of the straw itself (Song *et al.* 2023).

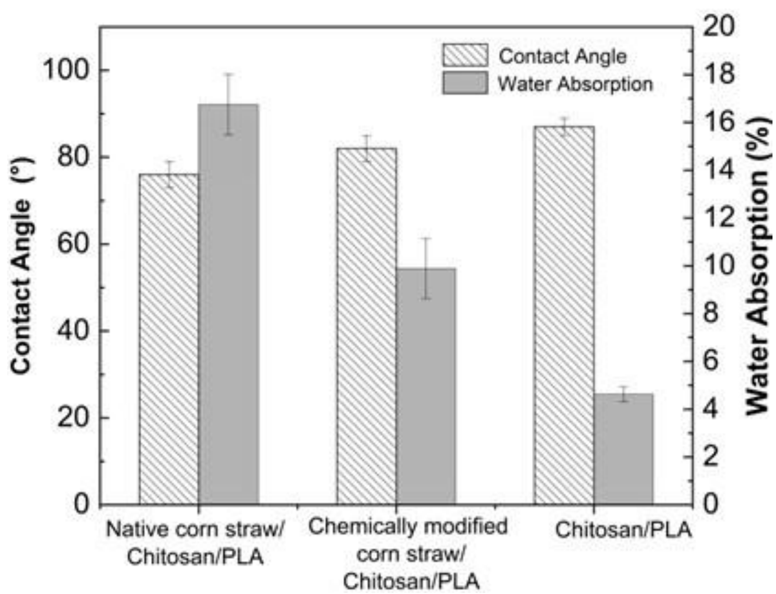


Fig. 8. Contact angle and water absorption properties of composites

Analysis of water absorption

Figure 8 also shows the water absorption result for chitosan/PLA, native corn straw/chitosan/PLA composites and chemically modified corn straw/chitosan/PLA composites. The water absorption performance of the chemically modified corn straw/chitosan/PLA composite (9.9%) was better than that of the native corn straw/ chitosan/PLA composite (16.8%).

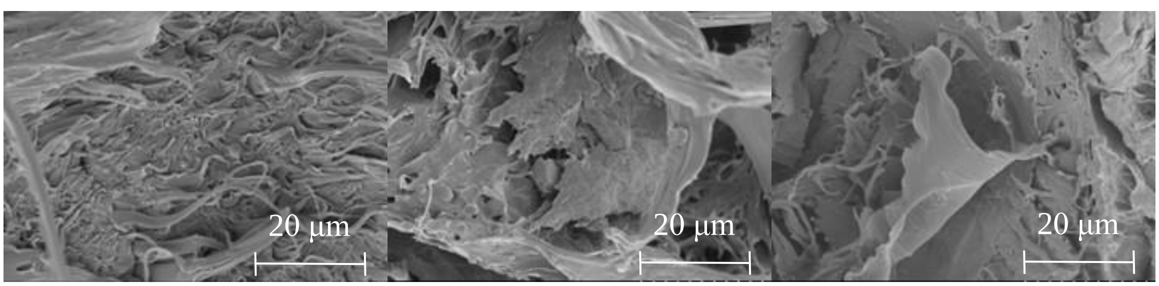
The water absorption of the chitosan/PLA was 4.62%. In general, the water absorption of composites could be increased by the presence of hydrophilic fiber materials (Huang *et al.* 2021). A possible explanation for this result was that the chemically modified corn straw was better dispersed in the polymer matrix, resulting in better water resistance and compatibility. This result was in agreement with the result of the contact angle analysis and with the result of the SEM shown below. Similar results have been published by Dixit and Yadav (2019).

Scanning electron microscopy

The surface morphology of the chitosan/PLA composites, native corn straw /chitosan/PLA composites, and chemically modified corn straw/chitosan/PLA composites are shown in Fig. 9. Micrographs of composite samples at 20 µm are shown. Figure 9a and 9b show that fewer surface cracks were visible in the chitosan/PLA composites than in the corn straw-based composites. Chitosan contains a hydroxyl group, which makes it behave like an amphiphilic polymer (Rizal *et al.* 2021).

Previous literature has reported the amphiphilic properties of chitosan. Fewer surface cracks, stronger adhesion, and more uniform distribution were observed in chemically modified corn straw in the chitosan/PLA polymer matrix (Fig. 9b and 9c). The NaOH modification could destroy the complex structure of the natural fiber to improve the evaluation and effectiveness of the fiber with polymers, which was confirmed by the higher mechanical strength in Fig. 10.

This result indicated an improvement in the miscibility between the treated biomass and the polymer matrix composite after hot pressing. Huang *et al.* (2021) in their publications showed similar results, that the polymer matrix bonded better to the alkali-treated straw than to the untreated straw.



(a) (b) (c)

Fig. 9. The surface morphology of composites (a: chitosan/PLA composite, 20µm; b: native corn straw/chitosan/PLA composites, 20µm; c: chemically modified corn straw/chitosan/PLA composites, 20µm)

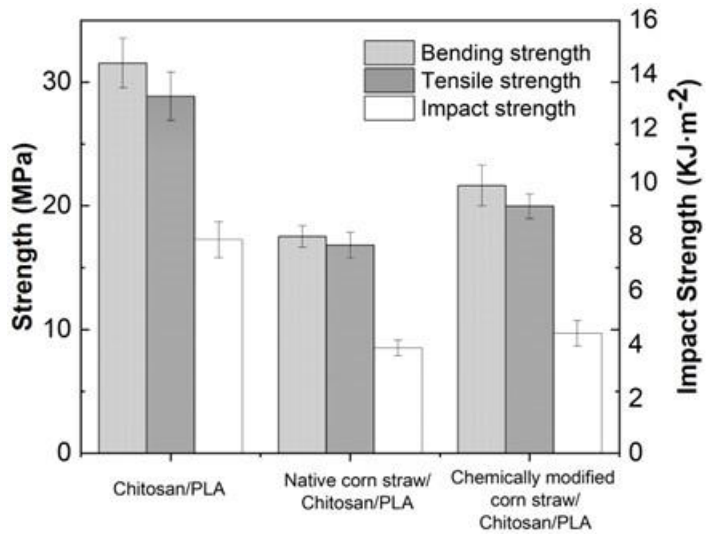


Fig. 10. Mechanical properties of composites

Mechanical properties of composites

The mechanical properties of the composites, including bending strength, impact strength and tensile strength, are shown in Fig. 10. The bending strength for chitosan/PLA, native corn straw/chitosan/PLA composites, and chemically modified corn straw/chitosan/PLA composites were 31.5, 17.5, and 21.6 MPa, respectively. The tensile strengths for the composites were 28.9 MPa, 16.8 MPa, and 20.0 MPa, respectively. In addition, the impact strengths for the prepared composite samples were 7.89, 3.89, and 4.43 kJ/m^2, respectively. Stronger adhesion and more uniform distribution between biomass and polymer were observed in the chemically modified corn straw bio-composite compared to the native corn straw-based composite, resulting in an improvement in the mechanical properties and quality of the bio-composite. The bending strength of the NaOH modified corn straw/chitosan/PLA based composite increased from 17.5 to 21.6 MPa (a 23.5% increase) compared to the native corn straw reinforced composite. Furthermore, the impact strength increased by 13.9% (from 3.89 to 4.43 kJ/m^2) after the blending of NaOH treated corn straw with chitosan/PLA.

A significant increase in tensile strength (18.7%) was observed after incorporation of NaOH treated corn straw with chitosan/PLA as compared to the native corn straw based composite. In addition, based on the published results (Daghigh *et al.* 2018; Sahai and Pardeshi 2019; Bahrami *et al.* 2021; Bahrami and Bagheri 2022), the modification of lignocellulosic fibers with silane coupling agents plays a beneficial role in improving the interfacial interaction and covalent bonding between hydrophilic fibers and hydrophobic polymer matrix. The compatibility between the hydrophobic polymer matrix and the hydrophilic fiber of the composite can be improved, thus improving the mechanical strength of the composite. Without the silane coupling agent treatment, large gaps may occur between the matrix and fiber, resulting in poor dispersion between the matrix and fiber. Improved mechanical properties for chemically modified corn straw in a chitosan/PLA polymer matrix, coupled with better suitability, demonstrating its potential for the preparation of novel eco-friendly composites.

CONCLUSIONS

1. Chemically modified corn straw was successfully incorporated into the poly(lactic acid) (PLA)/chitosan matrix for the synthesis of the optimized composite based on a Response Surface Methodology-Box Behnken design. The optimum mass fractions of chemically modified corn straw, chitosan and PLA for composites provided by RSM-BBD, namely 0.40 g chemically modified corn straw, 0.41g chitosan, and 3.00 g PLA, gave a bending strength of 21.0 MPa, which was in agreement with the experimental result. The results suggest that the mathematical model provided by Design Expert was both appropriate and reliable.
2. The novel composite prepared under the optimized factors was further characterized by Fourier transform infrared spectroscopy, contact angle test, water absorption test, scanning electron microscopy, and mechanical test. Mechanical strength including bending strength, impact strength and tensile strength of chemically modified corn straw based composites were 21.6 MPa, 4.43 kJ/m^2, and 20.0 MPa, respectively, which increased by 23.5%, 13.9%, and 18.7%, respectively compared to native corn straw based composite. The chemically modified corn straw/chitosan/PLA had a lower water absorption percentage of 8.48% weight gain after immersion in distilled water for 24 hours than the raw corn straw/chitosan/PLA. Results for contact angle increased by 6° for alkali-treated corn straw/chitosan/PLA compared with native corn straw based composite. Improved mechanical strength and hydrophobicity for chemically modified corn straw-based composites suggested the potential of chemically modified biomass fibers and bio-based degradable polymers to produce environmentally friendly polymer composites.

ACKNOWLEDGMENTS

This research was funded by the Natural Science Foundation of Hunan Province (Grant No. 2019JJ50678), the Hunan Educational Science Research Workers Association Project (Grant No. XJKX18B290), and the Ministry of Education Industry-School Cooperative Education Project (Grant No. 201901137029).

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Article submitted: August 9, 2023; Peer review completed: September 2, 2023; Revised version received and accepted: September 21, 2023; Published: October 5, 2023.
DOI: 10.15376/biores.18.4.7943-7962