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Article

Optimization of Lignin-Nanofiber-Filled Thermoplastic Starch Composite Film Production for Potential Application in Food Packaging

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Abstract: The optimization of production of lignin-nanofiber-filled thermoplastic starch composite film for potential application in food packaging was carried using Response Surface Methodology (RSM), through the adoption of the Box-Wilson Central Composite Design (CCD) with 1 center point. The effects of filler loading on moisture absorption (MAB), tensile strength [TS], percent elongation [PE] and Young's modulus [YM]) of the films were investigated in order to construct the desirability indices of the composite. The quality of the fitting model was expressed by the coefficient of determination, R^2 and the adjusted R^2. Results showed that the nanocomposite films were best fitted by a quadratic regression model with a high coefficient of determination (R^2) value. The selected film has desirability of 76.80 %, close to the objective function, and contained 4.81wt. % lignin and 5.00wt. % nanofibre. The MAB, TS, YM and PE of the selected film were 17.80 %, 21.51 MPa, 25.76 MPa and 48.81 %, respectively. The addition of lignin and nanofiber to starch composite reduced the moisture absorption tendency but increased the mechanical properties of the films due to the good filler/matrix interfacial adhesion. Conclusively, results suggested that these films would be suitable for packaging application.

Keywords: lignin; nanocomposite; nanofiber; optimization; percent elongation; starch; tensile strength; Young's modulus

1. Introduction

Synthetic plastics have dominated every field of human activity, particularly the packaging industries (Vert *et al.*, 2002). Despite their many merits, synthetic polymers have started becoming a major environmental concern for some time now. Due to the fact that they are non-biodegradable and also dependent upon non-renewable petroleum resource, the blooming usage of these plastics have caused grave energy crises as well as environmental pollution associated with their disposal, including damage to the eco-system, water supplies, sewer systems as well as rivers and streams. As a result, great attention is being drawn to natural polymers, e.g., starch, because they are inherently biodegradable, renewable, cost effective and available from many plants. In order to make it suitable for industrial application, such as packaging, starch is usually processed in the presence of a plasticizer to obtain a product called thermoplastic (TPS). However, TPS

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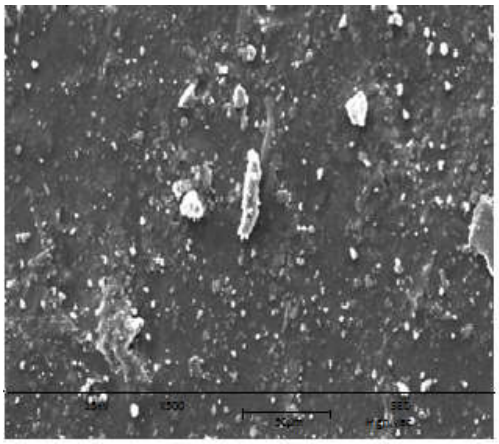
alone cannot be employed for packaging because they have low mechanical strength and high water sensitivity (Bhattacharya, 1998), which falls below the requirements of a packaging material. Therefore, there is the need for the incorporation of fillers to improve its properties (García *et al.*, 2009a; Siqueira *et al.*, 2009; Famá *et al.*, 2010; Fama *et al.*, 2011; Fama *et al.*, 2012). Lignin and nanofibers are potential fillers which are currently in great demand due to their natural abundance, being derived from plants, and susceptibility to biodegradability. So far, studies based on the simultaneous incorporation of lignin and nanofibers into thermoplastic starch composite film have not been reported in the literature. Further to this, information on the optimization of the experimental variables for the development of flexible films from starch for food packaging is limited hence, the justification for the present study. Therefore, the objective of this research is to produce lignin-nanofiber-filled thermoplastic starch composite film, with optimization of key process variables, for potential application in food packaging.

2. Results and Discussion

2.1. Film morphology

The SEM micrograph of the lignin-nanofiber-filled thermoplastic starch composite film is shown in **Figure 1**. The SEM micrograph showed that the fillers (lignin and nanofiber) were homogeneously distributed within the matrix of the starch nanocomposite film, a situation that usually results in improved mechanical properties. The white dots with varying sizes on the composite are considered as the fillers embedded in the starch matrix.



2.2. Development of regression model equations by Central Composite Design (CCD) for lignin-nanofiber-filled thermoplastic starch composite film

The quadratic models, in terms of actual factors used in achieving the desired optimum or ideal films, were obtained from analysis of variance (ANOVA) (**Tables 2-5**) and are given in **Equations 1 to 4**. The positive signs in the models indicate synergetic effects, whereas the negative signs, antagonistic effects. The model for predicting the moisture absorption capacity of the lignin-nanofiber-filled thermoplastic starch composite film in terms of actual factors is given in **Equation 1**.

$$MAB = 35.53 + 0.837l - 0.321n - 0.755ln \quad (1)$$

$$\langle R^2 = 91.02\ \% | {R_{adj}}^2 = 85.63\ \% | {R_{pred}}^2 = 64.30\ \% \rangle$$

Where: MAB = moisture absorption capacity, l = lignin (wt. %), n = nanofibre (wt. %)

The model was significant at p-value of 0.0048 and the coefficient of determination (R^2) of 0.9102 was obtained. This indicates that the statistical model could explain a 91.02 % of the variability, while the remaining 8.98wt. % could not be accounted for by the independent variables [8]. The predicted R^2 of 64.30 % agrees reasonably with adjusted R^2 (85.63 %) as should normally be the case for model adequacy due to very small blocking

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effect of the data used. The precision of the model is high since the adequate precision value obtained was ~11.156 [9].

The model for predicting the percentage elongation of the lignin-nanofiber-filled thermoplastic starch composite film in terms of actual factors is given in **Equation 2**.

$$PE = 50.35 + 0.10l - 1.09n + 0.077ln - 0.067l^2 + 0.124n^2 \quad (2)$$

$$\langle R^2 = 84.49\ \% | {R_{adj}}^2 = 58.65\ \% | {R_{pred}}^2 = -82.39\ \% \rangle$$

where: PE = elongation (wt. %), l and n retained their usual meaning

The model was significant at a p-value of 0.1792 and the coefficient of determination (R^2) of 0.8449 was obtained. This indicates that the model could describe 84.49wt. % variability while 15.51wt. % was inexplicable by the independent variables [8]. In addition, the negative predicted R^2 value of -82.39wt. % implied the fact that the fitted model, though precise (with adequate precision value of 5.37), is not a suitable predictor of the percentage elongation of the starch composite film.

The model for predicting the tensile strength of the lignin-nanofiber-filled thermoplastic starch composite film with respect to the actual factors is given in **Equation 3**.

$$TS = 17.32 + 0.37l + 0.48n \quad (3)$$

$$\langle R^2 = 83.46\ \% | {R_{adj}}^2 = 77.94\ \% | {R_{pred}}^2 = 61.72\ \% \rangle$$

Where: TS = tensile strength (MPa), l and n retained their usual meaning

The model was significant at p-value of 0.0045 and the coefficient of determination (R^2) of 0.8346 was obtained. This indicates that the statistical model could explain the 83.46 % value of the variability, while a 16.54 % value was inexplicable by the independent variables [8]. In addition, the predicted R^2 of 61.72wt. % agrees with the R^2 (adjusted) of 77.94 % as should normally be the case for adequate model. The model is precise in its capacity to predict the tensile strength of the starch mixture film since an adequate precision value recorded was 10.91 [9].

The model for predicting the Young's modulus of the lignin-nanofiber-filled thermoplastic starch composite film in terms of actual factors is given in **Equation 4**.

$$YM = 24.5 + 0.09l + 0.165n \quad (4)$$

$$\langle R^2 = 95.01\ \% | {R_{adj}}^2 = 93.34\ \% | {R_{pred}}^2 = 91.81\ \% \rangle$$

Where: YM = Young's modulus (MPa), l and n retained their usual meaning

The model was found to be significant at 0.0001 p-value and the coefficient of determination (R^2) of 0.9501 was, obtained. This indicates that the model could give explanation for 95.01 % of the variability while 4.99 % was inexplicable by the independent variables [8]. The predicted R^2 value, 91.81 % agrees reasonably with the R^2 adjusted of 93.34 % for adequate model and this was caused by small block effect of the data used in generating the model. In addition, the model is precise in its capability to forecast the lignin-nanofiber-filled thermoplastic starch composite film's young's modulus since the adequate precision recorded value was 20.51 [9].

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Table 2. ANOVA for response surface quadratic model for MAB of lignin-nanofiber-filled thermoplastic starch composite film.

Source	Sum of squares	df	Mean square	F value	p-value prob > F	
Model	245.9	3	81.97	16.89	0.0048	significant
A-Lignin	48.91	1	48.91	10.08	0.0247	
B-Nanofiber	160.52	1	160.52	33.08	0.0022	
AB	36.47	1	36.47	7.52	0.0407	
Residual	24.26	5	4.85			
Cor Total	270.17	8				
Std. Dev.	2.2		R-Squared	0.9102		
Mean	28.28		Adj R-Squared	0.8563		
C.V. wt. %	7.79		Pred R-Squared	0.643		
PRESS	96.44		Adeq Precision	11.156		

Table 3. ANOVA for response surface quadratic model for TS of lignin-nanofiber-filled thermoplastic starch composite film.

Source	Sum of squares	df	Mean square	F value	p-value prob > F	
Model	8.86	2	4.43	15.14	0.0045	significant
A-Lignin	3.27	1	3.27	11.18	0.0155	
B-Nanofiber	5.59	1	5.59	19.09	0.0047	
Residual	1.76	6	0.29			
Cor Total	10.61	8				
Std. Dev.	0.54		R-Squared	0.8346		
Mean	19.88		Adj R-Squared	0.7794		
C.V. wt. %	2.72		Pred R-Squared	0.6172		
PRESS	4.06		Adeq Precision	10.908		

Table 4. ANOVA for response surface quadratic model for YM lignin-nanofiber-filled thermoplastic starch composite film.

Source	Sum of squares	df	Mean square	F value	p-value prob > F	
Model	0.85	2	0.42	57.09	0.0001	significant
A-Lignin	0.2	1	0.2	26.37	0.0021	
B-Nanofiber	0.65	1	0.65	87.81	< 0.0001	
Residual	0.045	6	7.44E-03			
Cor Total	0.89	8				
Std. Dev.	0.086		R-Squared	0.9501		
Mean	25.26		Adj R-Squared	0.9334		
C.V. wt. %	0.34		Pred R-Squared	0.9181		
PRESS	0.073		Adeq Precision	20.514		

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Table 5. ANOVA for response surface quadratic model for PE of lignin-nanofiber-filled thermoplastic starch composite film.

Source	Sum of squares	df	Mean square	F value	p-value prob > F	
Model	1.43	5	0.29	3.27	0.1792	not significant
A-Lignin	0.11	1	0.11	1.22	0.3502	
B-Nanofiber	0.32	1	0.32	3.6	0.154	
AB	0.38	1	0.38	4.29	0.1302	
A^2	0.14	1	0.14	1.62	0.2922	
B^2	0.49	1	0.49	5.62	0.0985	
Residual	0.26	3	0.088			
Cor Total	1.69	8				
Std. Dev.	0.3		R-Squared	0.8449		
Mean	48.76		Adj R-Squared	0.5865		
C.V. wt. %	0.61		Pred R-quared	-0.8239		
PRESS	3.09		Adeq Precision	5.373		

2.3. Analyses of Response Surfaces

The 3D response surface plots of the joint effects of the independent variables (lignin and nanofiber) on the MAB, TS, YM and PE of lignin-nanofiber-filled thermoplastic starch composite film, as performed according to working conditions stated **Table 6** are presented in **Figure 2**. The 3D response surfaces were plotted in order to look into the probable interactions among the variables and also to determine the optimum conditions of each factor for minimum moisture absorption and maximum strength of the starch nanocomposite films.

Table 6. RSM factorial design matrix for lignin-nanofiber-filled thermoplastic starch composite film.

Run	Factors		Responses			
	Lignin (wt. %)	Nanofiber (wt. %)	MAB (%)	TS (MPa)	YM	PE (%)
1	3.0	1.0	32.558	18.370	24.960	49.300
2	1.0	3.0	31.818	19.250	25.050	48.250
3	1.0	1.0	32.787	18.070	24.800	49.650
4	5.0	3.0	28.571	21.510	25.520	48.525
5	3.0	5.0	22.034	20.510	25.675	49.000
6	5.0	5.0	15.590	20.980	25.740	48.575
7	5.0	1.0	31.884	19.750	25.100	48.500
8	1.0	5.0	28.571	20.490	25.425	48.500
9	3.0	3.0	30.693	19.970	25.100	48.500

The response surface plots for the influence of lignin and nanofiber contents on the MAB, TS, YM and PE of the lignin-nanofiber-filled thermoplastic starch composite film are presented in **Figure 2**.

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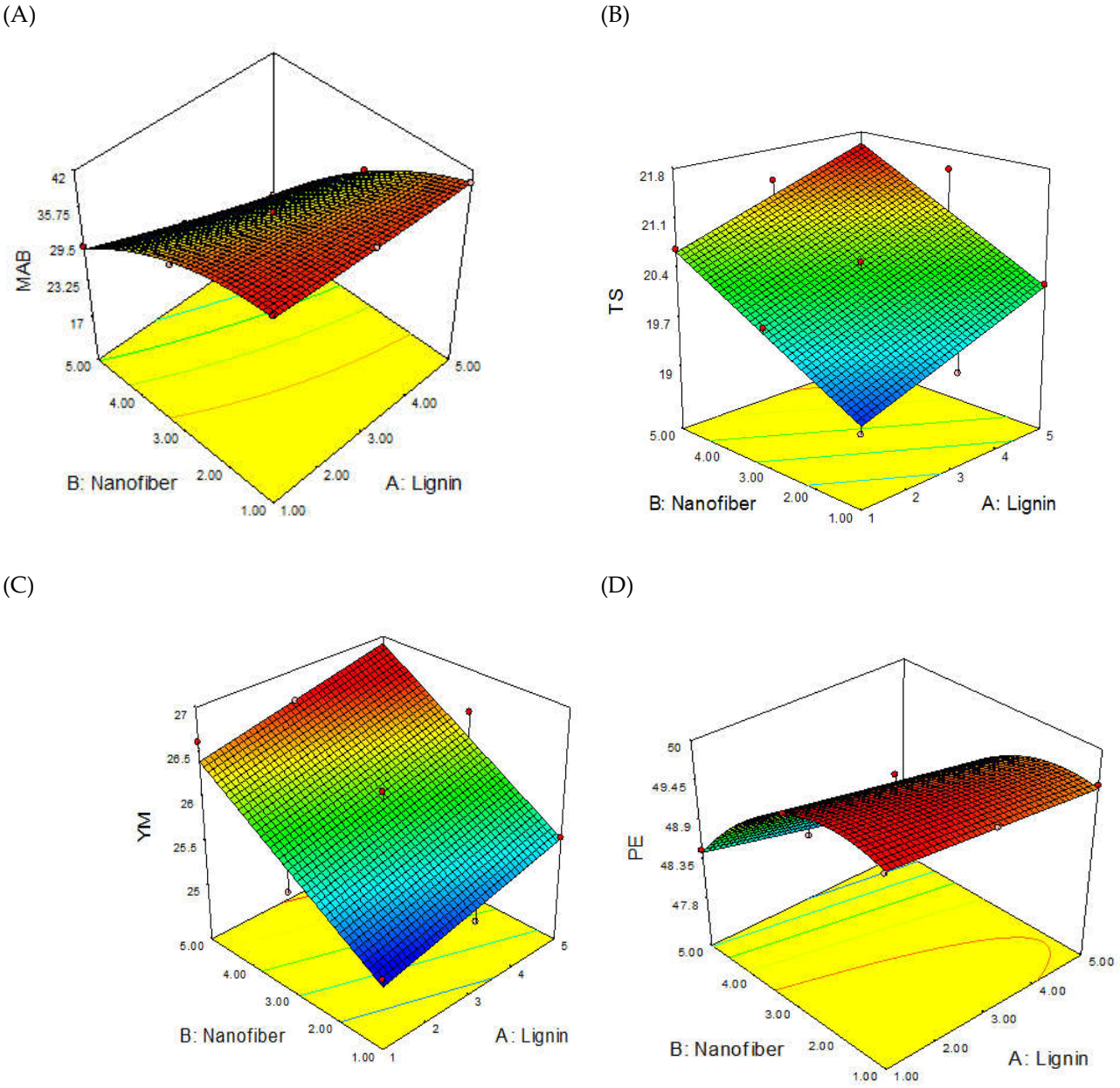

Figure 2. The influence of filler contents on (A) MAB (B) TS (C) YM and (D) PE of the lignin-nanofiber-filled thermoplastic starch composite film.

The results obtained revealed that the inclusion of nanofiber content had the most significant effect on the moisture absorption and mechanical properties of the lignin-nanofiber-filled thermoplastic starch composite film, followed by lignin inclusion content. The MAB reduced rapidly as nanofiber content increased when compared to that of lignin content. The lignin and nanofiber contents interacted negatively. This shows that the moisture absorption reduced as lignin and nanofiber contents increased. The decrease in MAB with increase in lignin and nanofiber contents was because of the strong filler-matrix interaction, which reduced the molecular mobility and diffusivity in the matrix material thus, limiting the degree of moisture uptake [10]. This result is in accordance with the findings of Khan *et al.* [11], Mitchelle [12], and Taghizedeh and Sabouri [13] who reported low moisture absorption rates for cocoyam, tapioca and modified corn starch films, respectively with increase in filler loading.

The results also showed that TS and YM of the starch nanocomposite film increased as the lignin and nanofiber contents increased while PE decreased with increase in lignin and nanofiber contents. The significant increase in TS and YM of the lignin-nanofiber-

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filled thermoplastic starch composite film with increase in filler contents, particularly nanofiber, was due to the small sizes (nano-range), smooth surface and large surface area of these fiber, which gave a good fiber/matrix interaction thus, improving the composite film's strength [14]. It might also be that lignin improved the compatibility between starch and nanofiber [15]. Besides, Suarez *et al.* [16] also reported the fact that a good interfacial region increases stress transfer efficiency from the matrix to the fillers thereby increasing the composite's strength.

This result corroborated with that of Wang *et al.* [15] who confirmed a rise in TS and YM, but a decrease in elongation-at-break, of a PLA nanocomposite reinforced with lignin-cellulose nanofiber (L-CNF) as the L-CNF content rose from 25 to 35wt. %. Patpen *et al.* [17] also reported the effect of cellulose addition on the TS of polylactic acid biocomposite; they observed an increase in this parameter as cellulose loading increased. Tawakkal *et al.* [18] also reported how kenaf derived cellulose (KDC) loaded polylactic affected the material's tensile properties and documented an improvement in both TS and tensile modulus as KDC loading increased from 30 to 60 wt. %. On the contrary, Sawpan *et al.* [19] studied the mechanical properties of hemp fiber-reinforced PLA biocomposites and established a non linear relationship between TS and fiber content, indicating that the strength of the biocomposite somewhat decreased as fiber content increased from 0 to 40 wt. %.

2.4. Optimization of lignin-nanofiber-filled thermoplastic starch composite film production

The result of the optimization of the experimental variables (lignin and nanofiber contents), showing the desirability function, with respect to the films prepared, is shown in **Figure 3**. The goal for both the water barrier and mechanical optimization was to minimize the moisture absorption and improve on the mechanical property; thus, the target value of the responses as obtained from the obtained experimental results was at the lowest and uppermost values, respectively. The result from the optimization showed that increases in the lignin and nanofiber contents, from 1 to 5wt. %, significantly affected the desirability of the films. Therefore, it is obvious from the optimization result that the selected film with desirability closer to the goal, is that one produced with the blend of 4.81wt. % lignin and 5.00wt. % nanofibre at 76.80 % desirability. The corresponding MAB, TS, YM and PE of the selected film, apparently the optimum sample, are 17.80 %, 21.51 MPa, 25.76 MPa and 48.81 %, respectively. This finding is similar to that of Wang *et al.* [15] who documented optimum values of 21.6 MPa and 21.6 % for the TS and elongation, respectively for PLA composites, reinforced with L-CNF. Akbar *et al.* [20], however, obtained optimum values of 50 MPa for the TS, 2.15MPa for the YM and 141.07 % for elongation, during the optimization of polyvinyl alcohol nanocomposite films. Patpen *et al.* [17] also reported an optimum value of 46.207 MPa, for optimization of PLA-based biocomposites reinforced with cellulose obtained from durian peel.

This study thus, affirms that lignin and nanofiber addition to starch composite minimised MAB and improved the mechanical properties of the produced films because of the good filler/matrix interfacial adhesion, as evident by the SEM micrograph. Hence, the produced films can be applied to package food.

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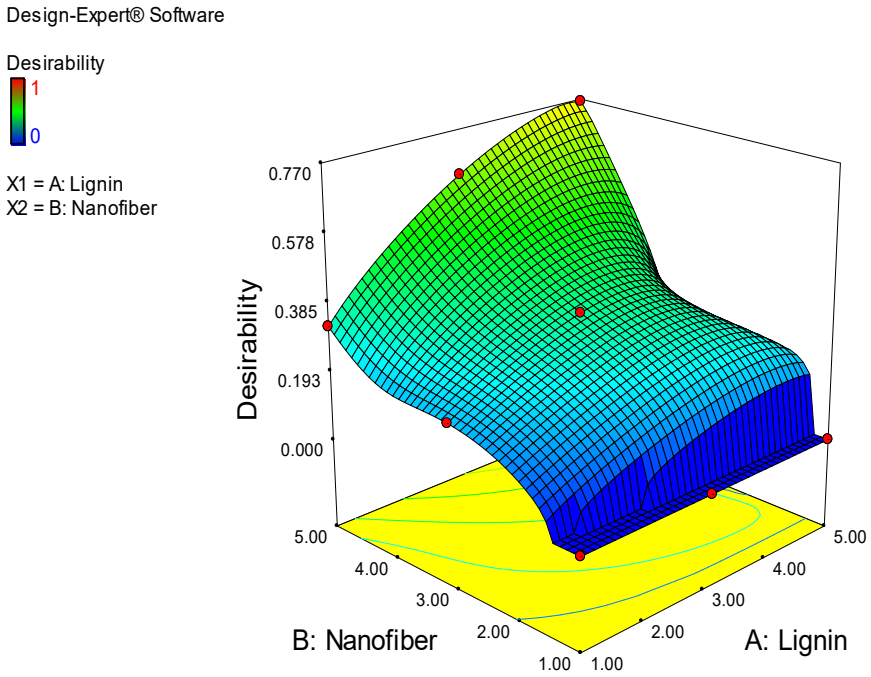

Figure 3. Desirability function of selecting the ideal film prepared.

3. Materials and Methods

3.1. Plant materials

Cassava (*Manihot esculenta* crantz) was bought from a farm in Minna, Nigeria, whereas bamboo (*Bambusa vulgaris* schrad) was collected from the river banks of Gurara in Izom, Niger State. They were identified and authenticated by a botanist at National Institute for Pharmaceutical Research and Development (NIPRD) Idu, Abuja. Specimen voucher numbers (NIPRD/H/6792 and NIPRD/H/6793), respectively, were placed at their herbarium for references in the future.

3.2. Chemicals

Analytical grade chemicals were employed for the study and include: ethanol (BDH chemicals, England), acetic anhydride (Sigma Aldrich), sodium hydroxide (Kermel, China), citric acid (BDH chemicals, England), hydrochloric acid (Griffin and George, England), sulphuric acid (BDH chemicals, England), hydrogen peroxide (BDH chemicals, England), Sodium sulphate (BDH chemicals, England), Ammonium hydroxide (Griffin and George, England) were purchased. Glycerol (BDH chemicals, England) was used as the plasticizer for the study.

3.3. Experimental design and optimization of starch nanocomposite film production

Design Expert software (version 7.0, Start-Ease Inc., Minneapolis, MN) was employed for the experimental design while Response Surface Methodology (RSM) was used for optimizing the conditions required for preparaing the starch nanocomposite films. As a result, 1 centre point Box-Wilson Central Composite Design (CCD) was utilized. After the designed experiment was performed, linear regression was then used to obtain results. The design consisted of 9 experimental runs. The RSM considered the effect of two variables: lignin content (wt. %) and nanofiber content (wt. %) used as fillers in the nanocomposite preparation with 5 levels each. The response functions measured were moisture absorption (MAB), tensile strength (TS), percent elongation (PE) and young's modulus (YM). Analysis of variances (ANOVA) was employed to analyse the obtained data in

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order to determine the interaction that exist between the process variables and the responses. Accurate and proper models were picked at $p<0.05$ and are said to have a significant model. The fitting model's quality was expressed by the coefficient of determination R^2 and adjusted R^2. The factors' level with their codings are shown in **Table 7**.

Table 7. Experimental variables and their coded levels of variables levels for CCD.

Variables	Units	Coded levels		
		-1	0	+1
Lignin	wt. %	1.0	3.0	5.0
Nanofiber	wt. %	1.0	3.0	5.0

In the optimization selection, two factors (lignin and nanofiber contents) were considered in order to build desirability indices. The objective was to reduce the MAB while improving TS, PE and YM; therefore, target value of responses was lowest value (for MAB) and highest values (for TS, PE and YM) from the experimental results obtained.

3.4. Preparation of lignin-nanofiber-filled thermoplastic starch composite film

Cassava starch (2 g) granules were dispersed in 50 ml distilled water and heat was applied at 70 °C for 20 min under constant stirring over a magnetic stirrer. Glycerol (50 wt. % based on dry cassava starch content) was added to the dispersion while the heating at 70 °C was continued, under constant stirring speed for next 2 min. Next, lignin and nanofiber (varied wt. %, with respect to the dry cassava starch content, and based on the statistical formulation of the Central Composite Design adopted) were added to the dispersion under the same conditions for another 2 min. Before being introduced into the plasticised starch mixture, the nanofibers were sonicated for 10 min by using a 60 W rated Sonicator. The mixture of dispersion was then cast into a mold and oven-dried at 50 °C using a still-air oven for 18 h in order to obtain dry lignin-nanofiber-filled thermoplastic starch composite films [21, 22], whose average thickness was found to be 0.12mm. The control (TPS) sample was also prepared using the same process mentioned above, except that there were no fillers added to it. All films were conditioned at 55 ± 5 % RH and 25 ± 2°C before testing their permeability and mechanical properties as described by the ASTM standard D882-09 [23] and Detduangchan *et al.* [24]. The conditioning was performed by inserting the films into desiccators containing saturated solution of $Mg(NO_3)_2 \bullet 6H_2O$ for 72 h. Part of the films were tested for water absorption, TS, PE and YM and the rest which were for other tests were kept in plastic bags and inserted into desiccators.

3.5. Characterization of lignin-nanofiber-filled thermoplastic starch composite film

Water absorption test

The film pieces (20 mm X 20 mm) were pre-conditioned by drying in the oven at 50 °C for 24 h and then weighed to determine the dry weight. They were then immersed in bath containing distilled water at room temperature. The film samples were removed from distilled water after intervals of 1, 3, 5, 7, 9 and 11 h and, after wiping off the excess water on their surfaces with tissue, their weights were determined. The water absorption capability (WAC) was thus calculated using **Equation 5** [21, 25]:

$$\text{WAC wt.\%} = \frac{(\text{Wwet} - \text{Wdry})}{\text{Wdry}} \text{ x } 100 \quad (5)$$

Where: Wwet = Wet specimen weight and Wdry represents the dry specimen weight.

3.6. Mechanical properties

The TS, PE and the YM values were determined with a universal testing machine (DBBMTCL-2500kg Testometric Rochdale, England) according to the ASTM D882 Standard [23]. Each sample, prior to testing, was conditioned at temperature of 25 °C and

relative humidity (RH) of 55 % for 24 hours prior to testing. The average thickness of the samples was about 0.12 mm. The tensile test was carried out using 1.3 mm/min crosshead speed. Each of the determinations was obtained from triplicate specimens.

3.7. Scanning electron microscopy (SEM)

The morphological structures of the lignin-nanofiber-filled thermoplastic starch composite films were determined using SEM (Zeiss Auriga HRSEM) at accelerating voltage of 15 kV. The samples as prepared were respectively placed on a stub with a double-sided adhesive tape after which, the samples were coated with a thin layer of gold. The micrographs were captured using a magnification of 350 times the original specimen size [22, 26].

3.8. Statistical analysis

Design Expert Software (version 7.0) was employed to analyze the obtained data. The determination of interaction effects between the factors and a quadratic surface plot was generated using Analysis of variance (ANOVA). The model adequacy was examined using the ANOVA, a normal probability plot and a residual plot according to method described in the literature [27]. An F-Test was also employed to determine the model's statistical significance and the regression coefficients' significance.

5. Conclusions

In conclusion, the film with desirability of ~76.80 %, which is closest to the objective function, and containing 4.81wt. % lignin and 5.00wt. % nanofiber was selected as the optimum sample. The MAB, TS, YM and PE of the selected film were 17.80 %, 21.51 MPa, 25.76 MPa and 48.81 %, respectively. This film presented the maximum mechanical potency and minimal moisture absorption capacity. The addition of lignin and nanofiber concurrently to the TPS matrix evidently caused a decrease in moisture absorption while at the same time an improvement in the mechanical properties of the films. Consequently, the prepared films have the potentials to be employed as films for packaging foods.

Author Contributions: Conceptualization and methodology were designed by Egwim, E.C. and Ochigbo, S.S. ; software, validation, by Egwim, E.C. and AbdulRasheed-Adeleke, T.; formal analysis, investigation, resources, data curation, and writing of original draft preparation, was done by AbdulRasheed-Adeleke, T.; writing—review and editing, by all.; visualization, supervision, and project administration were by Egwim, E.C. and Ochigbo, S.S.; funding acquisition, by AbdulRasheed-Adeleke, T. All authors have read and agreed to the published version of the manuscript.

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Sample Availability: Samples of the compounds are available from the authors.

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