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Optimization of Cellulose Acetate Production from Cellulosic Biomass: *Grevillea Robusta* Leaves

Catherine N. Muya[1,2,*], John M. Onyari[1], Lydia W. Njenga[1], Joab O. Onyango[2], Geoffrey Otieno[2], Bonface G. Mukabane[3]

[1]The University of Nairobi. Department of Chemistry, P. O. Box 30197-00100, Nairobi, Kenya
[2]Technical University of Kenya School of Chemistry and Material Science and Technology, P.O. Box 52428-00200, Nairobi, Kenya
[3]Nairobi Technical Training Institute, P. O BOX 30039-00100, Nairobi, Kenya
*Corresponding author: catherine.muya@tukenya.ac.ke

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Abstract Cellulose acetate was synthesized in a heterogeneous process from *Grevillea robusta* leaves. Cellulose fibers were extracted from the leaves and subjected to an optimized esterification process using response surface methodology (RSM). Glacial acetic acid was used as the solvent and acetic anhydride was used as the acetylating reagent with conc. H_2SO_4 as the catalyst. The achieved optimum percent weight gain (WPG) was 48.85 %, with a percent acetyl content (PAC) of 43.26 % and a degree of substitution (DS) of 2.82. Thermal gravimetric analysis (TGA), Scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) were utilized to analyze and evaluate the cellulose acetate that was synthesized. The XRD results gave X-ray diffraction patterns of the cellulose before and after acetylation. The diffraction patterns obtained indicated a decrease in crystallinity of the native cellulose compared to cellulose acetate. FTIR analysis established the formation of ester bonds in cellulose acetate. The SEM micrographs obtained were characteristic of the cellulose acetate standard used as the reference. The TGA and DTG analysis data indicated an increase in the thermal stability of acetylated cellulose compared to the extracted cellulose. The study suggests that *Grevillea robusta* leaves, which are renewable and readily available, non-wood biomass are a sustainable supply of affordable, high-quality cellulose that may be used to make cellulose acetate. The cellulose acetate produced can therefore be used to synthesize sustainable biodegradable polymers and biocomposites which will contribute to solving the serious environmental pollution problem due to petroleum-based plastic waste management.

Keywords: *Acetylation, Optimization, Cellulose acetate, Sustainable biodegradable polymers, Biomass*

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1. Introduction

The persistent environmental contamination caused by petroleum-based plastics due to their lack of degradation has resulted in the manufacturing of eco-friendly sustainable biodegradable materials. Sustainable biodegradable polymers are bio-tolerable, environmentally friendly substitutes, non-bioaccumulative, and biodegradable [1]. In addition, the Life Cycle Assessment verifies that biodegradable polymers extend the alternatives available for waste management treatment compared to conventional plastics, mainly municipal and residential composting as opposed to landfills [2].

The transformation of renewable resources into sustainable materials is an important step to achieving global sustainable development goals addressing the issues of resource efficiency, the economy, climate change, and the environment currently and in the future [3]. Biodegradable polymers are made using sustainable resources, including biomass such as crops and crop by-products, wood and wood wastes, and grasses.

Examples of bioplastics from biomass include polylactides, cellulose, starch, and soy-based plastics. Cellulose and its derivatives have become significant for their utilization in numerous domains of modern society, due to the high versatility, renewability, non-toxicity, and abundance of this natural polymer [4]. Cellulose is used to manufacture biopolymers from cellulose derivatives such as esters and ethers and to produce nanocellulose for pharmaceutical, military, design, and electronic fields [5].

Cellulose acetate is one of the most significant cellulose polymers. The benefits of cellulose acetate include its favorable physical and optical characteristics, high tensile strength, and thermoplastic with high stability. In addition, cellulose acetate is environmentally friendly because it is quickly degradable. It is applied in plastics, textile fibers, separation membranes, and medical and technological products. Food packaging frequently utilizes cellulose acetate since it is harmless [6].

Although cellulose-based products are environmentally beneficial, cellulose has drawbacks such as poor mechanical and barrier qualities in their intended use, poor solubility, and difficulties in solvent recovery [7,8]. These disadvantages limit the application of cellulose as a material for manufacturing products such as bioplastics and therefore need to be solved. The properties of cellulose and its processability can be improved by chemical and physical treatments forming cellulose derivatives. Acetylation is a chemical treatment commonly utilized to enhance cellulose compatibility and solvent dispersion by forming cellulose acetate [9].

Cellulose acetate is the most frequently applied cellulose ester (CA). It is prepared homogeneously or heterogeneously with acetic acid solvent and an excess acetic anhydride as the acetyl donor in the presence of a catalyst such as iodine and sulphuric acid [10,11]. The acetylation process modifies the structure of cellulose by substituting acetyl groups for its hydroxyl groups. This reduces the hydrophilicity of cellulose and hence improves its solubility in organic solvents [12]. The amount of hydroxyl groups substituted during the reaction can be determined using the degree of substitution (DS) and the percentage of acetylation. The average number of substituents per anhydroglucose unit, or DS, can range from 0 (for cellulose) to 3 (for cellulose triacetate). The resultant DS greatly impacts the final material qualities [13]. The accurate determination of DS is important to evaluate relationships between the structure and properties in designing the related targeted material property [14]. For instance, as the DS increases the biodegradability decreases [13]. Cellulose acetate is classified into three groups based on the extent of substitution: cellulose triacetate (CTA), cellulose diacetate (CDA), and cellulose monoacetate (CMA) [15].

Cellulose monoacetate (CMA) is formed when only one hydroxyl group in cellulose is changed to an acetyl group. CMA has a degree of substitution of 0 to 2 with acetyl groups less than 36.5 % [6]. The most predominant types of cellulose acetate are cellulose diacetate with DS of 2 to 2.5, [16] and cellulose triacetate with DS of 2.7 to 3. However, the DS of cellulose acetate is reduced through partial hydrolysis of cellulose triacetate from three acetyl groups per cellulose to two acetyl groups [10,17]. The crystallinity of cellulose triacetate is very high, which decreases in cellulose diacetate and finally in cellulose monoacetate [16].

Purified cellulose, mostly derived from wood pulp and cotton linters, is used in the commercial production of cellulose acetate. However, even while market demand is continuously rising, the usage of wood has become more and more restricted due to the requirement for the preservation and conservation of natural resources. Therefore, to get an appropriate grade of cellulose for industrial application, Numerous novel low-cost or low-value cellulose sources, primarily agricultural non-wood residuals, have been investigated [2,18].

Grevillea robusta fall leaves are used in this study as a suitable alternative renewable resource for optimal cellulose acetate production through an optimized synthetic process. *Grevillea robusta* is commonly known as silky oak. It generates a substantial quantity of leaf biomass quickly. Its capability to flourish in coffee and tea farms gives it an added benefit by providing the necessary humus and shade without interfering with nearby plants. The tree is widely grown and does well in a wide range of environmental conditions. This indicates that a large amount of biomass can be obtained from *Grevillea robusta* annually, supplying the polymer industry with urgently needed renewable raw materials.

2. Materials and Methods

2.1. Chemicals and Reagents

Fall leaves of *Grevillea robusta* were gathered at random from the tree plantation of the Kenya Forest Research Institute (K.E.F.R.I.) Muguga Centre, Nairobi, **Kenya** located on the map at (S 1^{0}17’ 31.4376$^{’’}$, E 36^{0}49’ 19.0056’’).

The reagents used in this study include sodium hydroxide (NaOH, 99.5%) and sodium hypochlorite (NaOCl, 10%) from Euro Chemicals Ltd. Kenya. Anthraquinone ($C_{14}H_8O_2$, 98%), from Loba Chemie Ltd, India. Potassium bromide (KBr, 99%) from High Pure Laboratory Chemicals Pvt. Ltd. Standard cellulose from Balston Ltd, England. Glacial acetic acid and acetic anhydride from Merck KGA, Germany. Sulphuric acid and standard cellulose triacetate from Sigma Aldrich. Acetone 99.5 % from Scharlab S. L. Spain and chloroform 99 % from Griff chem fine Chemicals India. These reagents were used as received.

2.2. Cellulose Extraction from Fall Leaves of *Grevillea robusta*

Alkaline delignification using sodium hydroxide and anthraquinone as redox catalyst was carried out in a water bath at 100 ± 5°C to isolate the cellulose from the hemicellulose and lignin present in the leaves. The delignification of biomass is essential in the synthesis process of cellulose acetate because lignin competes with cellulose for acetylation reactants [6]. A central composite design (CCD) of response surface methodology (RSM) was used to optimize cellulose extraction as described in our earlier work [18]. The ground clean dry leaves were treated with 14.6% NaOH solution and 0.1% anthraquinone charge for about 2.5 hours. The pulp was then bleached with 10% NaOCl for 2 hours. Distilled water was used to wash the bleached cellulose until the pH was about neutral and then dried at 105°C to constant weight.

2.3. Production of Cellulose Acetate

The cellulose acetylation process was performed using conc. sulphuric acid as a catalyst, acetic anhydride as the acetyl donor, and glacial acetic acid as an activating solvent. However, factors including catalyst concentration, temperature, and reaction time affect the reaction outcome. In this study, 5 grams of the cellulose was dispersed in glacial acetic acid and reacted with acetic anhydride in a fixed ratio of 1: 17.5: 5 respectively with continuous stirring. The reaction conditions were varied as follows: Conc. H_2SO_4 catalyst concentration (1 to 6 %), temperature (40 to 60°C), and the reaction time (2 to 3 hours). Initially in the activation stage, the glacial acetic acid was added to cellulose, and the mixture was heated to 40°C with continuous stirring for 30 minutes. This causes the swelling of cellulose fibers, which exposes the hydroxyl groups and consequently increases the activation of cellulose pulp for acetylation reactions. The acetylation process involved the addition of conc. H_2SO_4 catalyst and acetic anhydride (Table 1 and 2). The reaction continued at respective temperatures with constant stirring. The cellulose acetate produced was precipitated, by the addition of water. Following filtration, distilled water was used to wash the acetate to near-neutral pH. It was then dried in the oven at 60°C until constant mass.

2.3.1. Weight Percent Gain Determination

The weight gain is the difference between the weight of the cellulose used and the weight of the cellulose acetate produced after acetylation. This is required to ascertain the effectiveness of the acetylation process.

Equation 1 was used to calculate the weight percent gain (WPG) [19].

$$\text{Weight Percent Gain} = \frac{\left(W_{final} - W_{initial}\right)}{W_{initial}} \times 100 \qquad (1)$$

where $W_{initial}$ is the weight of dried cellulose and W_{final} is the weight of dried cellulose acetate.

2.3.2. The Determination of the Degree of Substitution and the Percentage Acetylation

The percentage of acetyl groups substituted by the hydroxyl groups in cellulose is known as percentage acetylation. Using Candido and Goncalves' approach, the percentage of acetylation and degree of substitution were computed [9]. Approximately 0.1 g of cellulose acetate was put in a conical flask, and soaked with 5 mL of 0.25 M NaOH solution and 5 mL of ethanol for 24 hr. Then 10 mL of 0.25 M HCl was added under stirring and the mixture left for 30 min. Subsequently, the mixture was titrated using 0.25 M NaOH solution. Phenolphthalein was used as an indicator. The percentage of the acetyl content (PAC) was calculated as shown in Equation 2.

$$PAC = \frac{\left[\left(V_{bi} + V_{bt}\right) \times \mu b - \left(V_a \times \mu a\right)\right] \times M}{W} \times 100 \qquad (2)$$

where V_{bi} —is the initial volume of NaOH added (L), V_{bt} —is the volume of NaOH used in titration (L), μb—molarity of NaOH, V_a —the volume of HCl added to the mixture (L), μa—molarity of HCl, M – Molar mass of acetyl group (43 g/mol), W—the weight of the sample (g)

The degree of substitution (DS) was calculated using Equation 3 [2,21].

$$DS = \frac{162 \times \%\ Acetyl}{\left[4300 - \left(42 \times \%\ Acetyl\right)\right]} \qquad (3)$$

2.4. Experimental Design and Optimization

Central Composite Design (CCD) of Response Surface Methodology (RSM) of design-expert version 13.0 software by Stat-Ease, Inc. USA. was used to study the best operating conditions to optimize cellulose acetate production. The RSM approach is economical and saves time compared to the traditional One-factor-at-a-time (OFAT) optimization method. The RSM establishes a factual correlation between the process variables and the expected outcome, through statistical and mathematical analysis. The CCD levels of the independent factors are shown in Table 1.

2.4.1. Suggested Model

The WPG, PAC, and DS were taken as the responses, and a second-order polynomial model was developed for the three factors. The model is shown in Equation 4.

$$Y_n = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} X_i X_j + \sum \beta_{ii} X_i^2 \qquad (4)$$

Where is the predicted response, β_0 is a constant, β_i is the linear regression coefficient, β_{ij} is the interaction coefficient, β_{ij} is the squared coefficient, X_i and X_j are the input variables.

The system represented by independent variables along with dependent outputs was modeled using analysis of variance, and the system was optimized by estimating the statistical parameters [22].

2.5. Characterization of Prepared Cellulose Acetate

2.5.1. Chemical Functional Group Analysis

A Nicolet Magna-IR 560 spectrometer was used to acquire infrared spectra. It encompassed 32 scans in micro-ATR mode with a resolution of 2 cm^{-1}. The finely ground sample was mixed with potassium bromide to form a pellet. Analysis of the FTIR spectrum was carried out in the wave number range of 400–4000 cm^{-1}.

Table 1. The CCD independent variables' levels

		Levels				
Independent variables	**Code**	**−α = -1.682**	**Low (-1)**	**Center (0)**	**High (+1)**	**+α = 1.682**
Conc. H_2SO_4%	A	0.6364	2.00	4.00	6.0	7.3636
Reaction time hrs.	B	1.6589	2.00	2.5	3.0	3.3409
Temperature ℃	C	33.1821	40	50.0	60.0	66.8179

2.5.2. The Crystal Structure Analysis

The XRD data for the samples was collected at 30 kV and 10 mA using a Bruker D2 Phaser diffractometer that was equipped with a high-speed linear detector (LYNXEYE) and Cu Kα radiation (λ = 1.54184 Å). At a scan speed of 1 s/step and a step size of 0.02°, the measurements were carried out at room temperature spanning the 2θ range of 2.5° to 80°. GSAS-II (General Structure Analysis System) software was used to perform the Rietveld analysis by applying the Rietveld technique [23]. The following formula represented in Equation 5 was used for calculating the sample crystallinity index:

$$\mathit{Crystallinity\ index} = \frac{\mathit{Area\ of\ crystalline\ peaks}}{\mathit{Area\ of\ the\ total\ domain}\left(\mathit{crystalline\ and\ amorphous\ peaks}\right)} \times 100 \tag{5}$$

2.5.3. Thermogravimetric Investigation

The thermal degradation characteristics of the produced cellulose acetate were analyzed using 10 mg of the sample on a TGA Q500 1732. The sample was heated from 50 – 900°C at 10°C/min. Every measurement was performed in a nitrogen atmosphere at a flow rate of 100 milliliters per minute.

2.5.4. The Cellulose Acetate Morphological Analysis

The surface morphology of the samples was observed using a scanning electron microscope (SEM), Tescan Vega 3 LMN, operating at a 20Kv accelerating voltage, employing a secondary electron detector (SED) and energy dispersive spectroscopy (EDS). The samples were placed on the aluminum stub and incubated in the oven at 60°C. The samples were gold sputtered to avoid overcharging. The effects of several chemical processes were assessed using a comparative analysis of extracted and acetylated cellulose.

3. Results and Discussion

The photographs of *G. robusta* ground leaves, extracted cellulose, and the cellulose acetate obtained in the study are shown in Figure 1. The extracted cellulose was a white fluffy material while the obtained cellulose acetate was a white fine powder.

3.1. Optimization of the Acetylation Process

By analyzing the impact and interactions of the process factors, the most favorable conditions for the synthesis of cellulose acetate were identified. The process factors include; concentration of H_2SO_4 acid (A), reaction time (B), and the temperature (C) over the observed responses; weight percent gain (WPG), percent acetyl content (PAC), and the degree of substitution (DS) using the surface response methodology. The whole central composite design (CCD) matrix and the experimental responses are shown in Table 2.

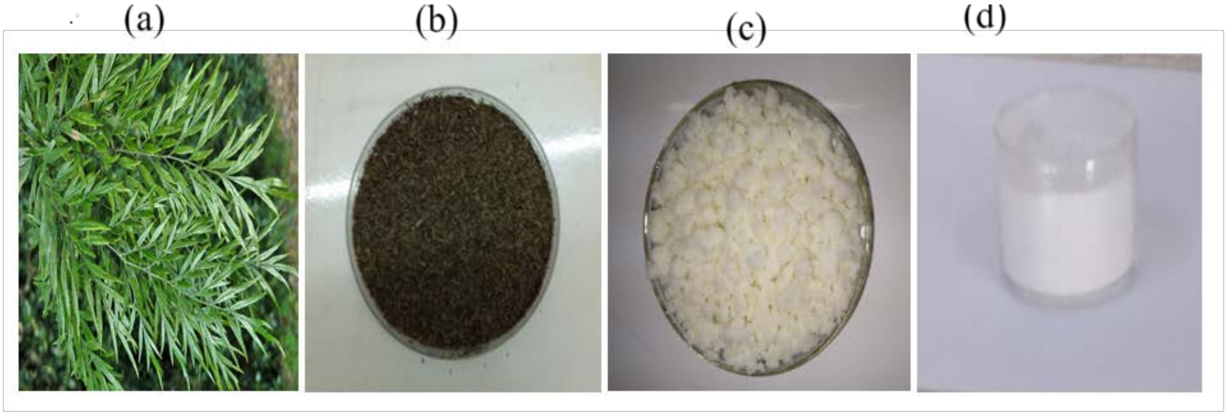

Figure 1. (a) *G. robusta* leaves, (b) ground leaves, (c) extracted cellulose, and (d) prepared cellulose acetate

Table 2. Central composite design for cellulose acetate preparation and the observed responses

Run	Level of Factors			Experimental responses		
	Factor 1	Factor 2	Factor 3	Response 1	Response 2	Response 3
	A: Conc. of H_2SO_4	B: Reaction time	C: Temperature	Weight Percent Gain (WPG)	Percent Acetyl Content (PAC)	Degree of Substitution (DS)
	%	Hrs.	℃	%	%	au
1	4	1.66	50	45.97	39.82	2.46
2	6	2	60	39.37	39.42	2.415
3	4	2.5	50	48.614	42.79	2.77
4	4	2.5	50	48.56	42.69	2.764
5	4	2.5	50	48.53	42.87	2.78
6	4	3.34	50	43.69	38.41	2.32
7	4	2.5	66.82	41.68	38.23	2.299
8	2	2	40	44.69	34.75	1.981

Run	Level of Factors			Experimental responses		
	Factor 1	Factor 2	Factor 3	Response 1	Response 2	Response 3
	A: Conc. of H_2SO_4	B: Reaction time	C: Temperature	Weight Percent Gain (WPG)	Percent Acetyl Content (PAC)	Degree of Substitution (DS)
9	0.64	2.5	50	38.47	24.11	1.07
10	6	3	60	39.01	37.55	2.211
11	4	2.5	50	48.84	42.74	2.764
12	2	3	40	42.46	34.63	2.02
13	2	2	60	43.12	31.49	1.71
14	6	2	40	45.62	39.66	2.44
15	4	2.5	50	48.56	42.68	2.757
16	2	3	60	40.35	30.02	1.6
17	6	3	40	45.67	39.24	2.397
18	4	2.5	50	48.76	42.76	2.766
19	4	2.5	33.18	48.44	42.23	2.71
20	7.36	2.5	50	38.11	34.46	1.957

Table 3. Analysis of variance (ANOVA)

	Weight Percent Gain	Percent Acetyl Content	Degree of Substitution
Std. Dev.	0.1369	0.0738	0.0085
Mean	44.43	38.03	2.31
C.V. %	0.3081	0.1941	0.3668
R^2	0.9994	0.9999	0.9998
Adjusted R^2	0.9988	0.9998	0.9997
Predicted R^2	0.9968	0.9995	0.9991
Adeq Precision	107.9083	357.6412	284.2176

Table 4. The F-value and p-value for the quadratic model, factors, and responses

Source	Weight Percent Gain (WPG)		Percent Acetyl Content (PAC)		Degree of Substitution (DS)		
	F-value	p-value	F-value	p-value	F-value	p-value	
Model	1711.93	< 0.0001	10131.13	< 0.0001	6499.38	< 0.0001	significant
A-Conc. of H_2SO_4	9.45	0.0117	24135.27	< 0.0001	13544.88	< 0.0001	
B-Reaction time	326.76	< 0.0001	524.98	< 0.0001	312.49	< 0.0001	
C-Temperature	3054.62	< 0.0001	3669.38	< 0.0001	2589.57	< 0.0001	
AB	146.73	< 0.0001	11.24	0.0073	53.95	< 0.0001	
AC	568.30	< 0.0001	809.15	< 0.0001	401.26	< 0.0001	
BC	6.02	0.0340	179.79	< 0.0001	167.36	< 0.0001	
A^2	10106.86	< 0.0001	59794.52	< 0.0001	39462.21	< 0.0001	
B^2	1325.64	< 0.0001	4333.01	< 0.0001	3575.13	< 0.0001	
C^2	1166.51	< 0.0001	2075.31	< 0.0001	1734.96	< 0.0001	
Lack of Fit	1.35	0.3762	1.22	0.4162	1.42	0.3554	not significant

3.1.1. Analysis of Variance (ANOVA)

The data in Table 2 was subjected to ANOVA and the results are shown in Table 3. The predicted R^2 of 0.9968 is close to the adjusted R^2 of 0.9988 for weight percent gain as well as that of 0.9995 to 0.9998 for percent acetyl content and 0.9991 to 0.9997 for the degree of substitution, indicating that the model is significant [19].

The model p-values for WPG, PAC, and DS are less than 0.05, implying that they are significant, as indicated in Table 4. The Lack of Fit p-value of 0.3762 for WPG, 0.4162 for PAC, and 0.3554 for DS demonstrates that compared to the pure error, the Lack of Fit is not significant, which is favorable for the model [24].

The p-values in Table 4 imply that factors A, B, C, AB, AC, BC, A^2, B^2, and C^2 are significant model terms for the PGW, PAC, and DS.

The WPG, PAC, and D S were taken as the responses, and the developed second-order polynomial models for the three factors are given in equations 6, 7, and 8 respectively.

$$\begin{aligned} WPG = {} & 48.64 - 0.1139A - 0.6696B - 2.05C + 0.5863AB \\ & - 1.15AC - 0.1187BC - 3.63A^2 - 1.31B^2 - 1.23C^2 \end{aligned} \tag{6}$$

$$\begin{aligned} PAC = {} & 42.75 + 3.1A - 0.4577B - 1.21C - 0.0875AB \\ & + 0.7425AC - 0.35BC - 4.76A^2 - 1.28B^2 - 0.886C^2 \end{aligned} \tag{7}$$

$$\begin{aligned} DS = {} & 2.77 + 0.2668A - 0.0405B - 0.1167C - 0.022AB \\ & + 0.06AC - 0.03288BC - 0.4433A^2 - 0.1334B^2 - 0.093C^2 \end{aligned} \tag{8}$$

3.1.2. Interactive Effects of the Process Factors on Weight Percent Gain (WPG)

The three-dimensional plots depicted in Figure 2 were generated to assess the impacts of the process variables temperature, reaction time, and H_2SO_4 concentration.

The H_2SO_4 concentration and reaction time significantly affected the WPG as shown in Figure 2(a). There was an increase in WPG with a catalyst concentration increase of 5 percent. The reaction time displayed a major influence on WPG which increased up to a reaction time of 2.7 hours and then started to decrease. Based on the high reactant concentration, the reaction rate was initially high. Towards the end of the reaction, WPG decreased due to the low concentration of reactants as more cellulose was already acetylated. According to Egot and Alguno (2018) [21], longer reaction times are also known to cause degradation and hydrolysis of cellulose acetate. The temperature had little effect on WPG, however, higher temperatures from 50 to 60°C led to a decrease. High catalyst loading and high reaction temperatures lead to a reduction in WPG due to the degradation of carbohydrates mainly cellulose to smaller soluble molecules [25].

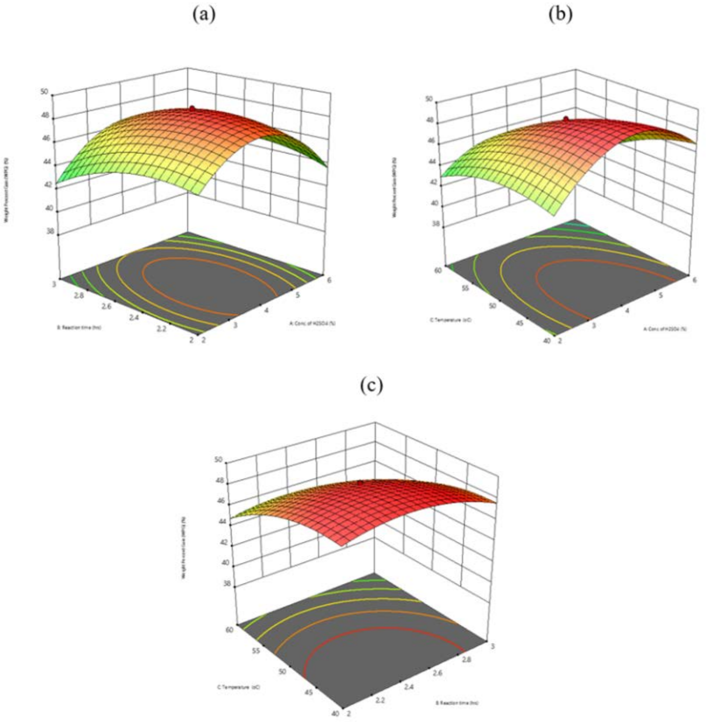

Figure 2. 3-D surface plots showing the WPG as a function of the following variables: (a) catalyst concentration and reaction time; (b) catalyst charge and temperature; and (c) time of reaction and temperature

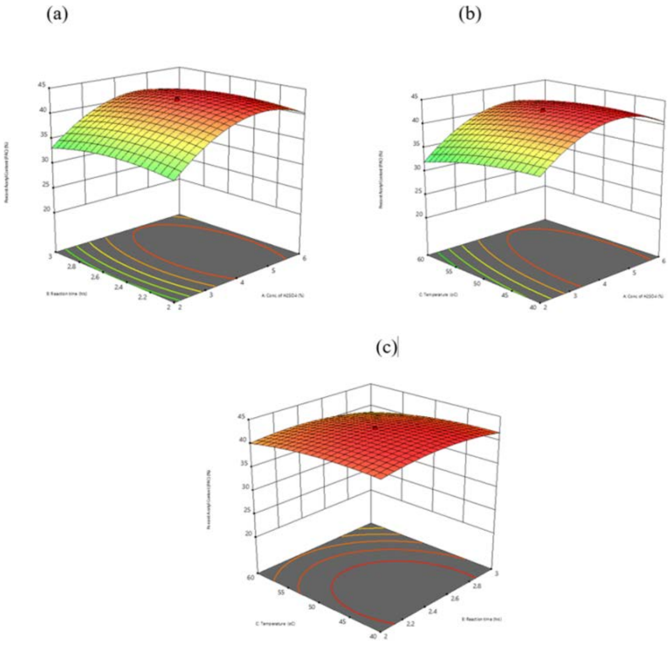

Figure 3. 3-D surface plots of the PAC as a function of (a) catalyst charge and reaction time, (b) catalyst charge and temperature, and (c) reaction time and temperature

3.1.3. Interactive Effects of the Process Factors on Percent Acetyl Content (PAC)

The interactive effect of the catalyst charge, reaction time, and temperature on the acetyl content of the prepared cellulose acetate was evaluated by plotting the 3-D surface plots as shown in Figure 3.

The PAC was greatly influenced by the catalyst charge and reaction time. This is because the catalyst lowers the activation energy resulting in a faster reaction of the substitution of the hydroxyl groups with acetyl groups over time. The highest PAC of 42.87 % was attained at a catalyst concentration of 4 %, reaction time of 2.5 hours, and temperature of 50°C. The increase in temperature led to a slight rise in PAC as was also observed by Bello et al. (2016) in the acetylation of cotton stalks [19].

3.1.4. Interactive Effects of the Process Factors on Degree of Substitution (DS)

The effect of process factors had almost a similar effect on DS as on PAC as shown in Figures 4 and 3 respectively. This is mostly because the two are related. Catalyst charge and reaction time significantly influenced DS as PAC. The increase in catalyst charge and reaction time resulted in an increase in DS as more hydroxyl groups were replaced by the acetyl groups due to low activation energy and prolonged period of reaction. Similar results were observed by Jassem et al. (2020), where the PAC and consequently DS of cellulose acetate produced from date palm fronds increased with prolonged reaction time [16]. At catalyst loading of 4 % and 50°C with a reaction time of 1.66 hours, the attained DS was 2.5. At a reaction time of 2.5 hours, DS was 2.78 and a further increase in reaction time to 3.34 hours gave a reduced DS of 2.32. The temperature, though with a slight influence on the reaction output, has a major role in affecting the mobility of crystallites enhancing the acetylation reaction [19].

3.1.5. Results of the Model Optimization and Validation

The obtained model results in this study were optimized by the desirability function [24]. The predicted optimum responses were; WPG of 49.33 %, PAC of 43.52 %, and DS of 2.83 at reaction conditions of 4.64 % catalyst charge, 2.43 hours, and temperature of 43.31 ℃. Experiments in triplicate validated the optimization result. The obtained results were 48.85% WPG, PAC of 43.26 %, and DS of 2.82. The attained results demonstrate the appropriateness and precision of the model since the difference between the obtained and the anticipated results is within acceptable limits. This CA was characterized as cellulose triacetate. It was completely soluble in chloroform but partly soluble in acetone probably because it was not fully acetylated as shown in Figure 5.

Cellulose acetate with DS of 0.6 – 0.9 is soluble in water, DS of 1.2 – 1.8 is soluble in 2-Methoxy ethanol, DS of 2.2 – 2.7 is soluble in acetone, and that with DS of 2.8 – 3.0 is soluble in chloroform [26].

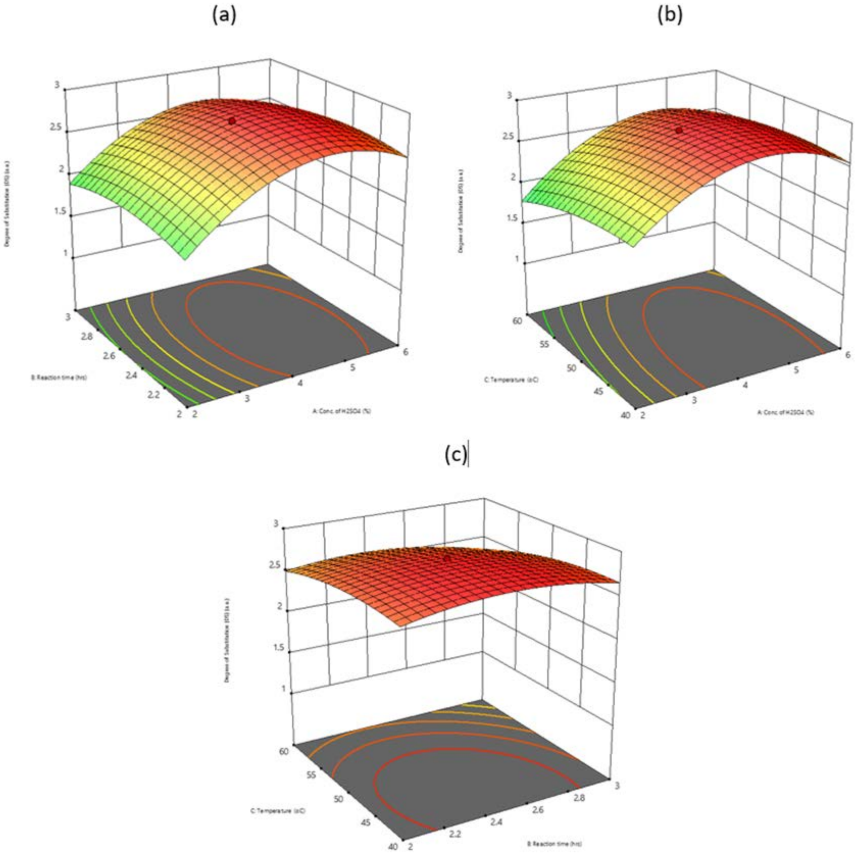

Figure 4. 3-D surface plots of the DS as a function of (a) concentration of the catalyst and reaction time, (b) concentration of catalyst and temperature, and (c) reaction time and temperature

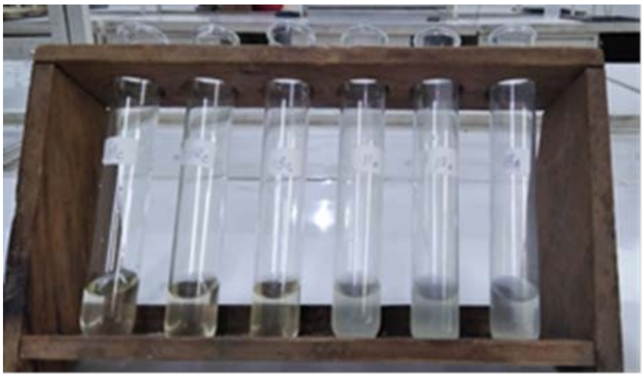

Figure 5. Solubility of the prepared cellulose acetate: (the 3 samples to the left) in chloroform and (the 3 samples to the right) in acetone

3.2. FT-IR Spectral Analysis

The conspicuous band in cellulose about 3550 -3067 cm^{-1} caused by the hydroxyl groups stretching vibrations drastically decreased with the acetylation reaction, according to the FTIR spectra shown in Figure 6. This results from the acetyl groups in cellulose acetate replacing the hydroxyl groups, similar results were observed by Egot and Olguno (2016) [21]. The formation of cellulose acetate was observed by the ester carbonyl (C=O) absorption peak at 1742.8 cm^{-1} and the carbonyl hydrogen (C-H) peak at 1374.88 cm^{-1} in the acetyl group. This is further verified by the presence of the absorption peak of (C-O) in the O-C=O group at 1225.12 cm^{-1} [19]. The peak at around 1030.92 cm^{-1} was caused by the ether bond of the glycoside unit. The prepared CA displayed similar and enhanced characteristic peaks in comparison with the standard CA. The developed spectral analysis therefore confirmed the acetylation of the extracted cellulose from *G. robusta* leaves.

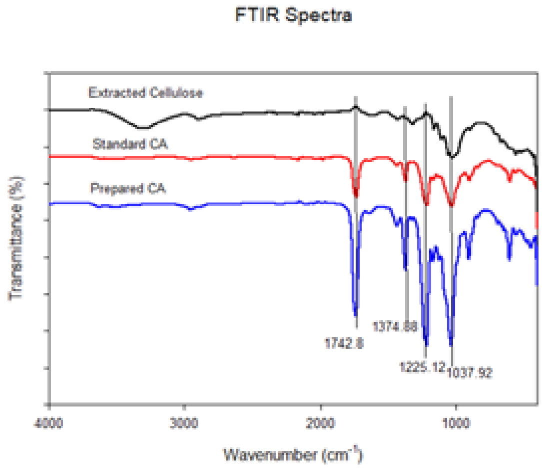

Figure 6. FTIR spectra for the extracted cellulose, prepared cellulose acetate, and standard cellulose acetate

3.3. X-Ray Diffraction Analysis

The prepared cellulose acetate, just like the standard exhibits less crystallinity compared to cellulose as shown in Figure 7. This is evident due to the decrease in the magnitude of the crystalline peak at 2 around 22^0 in cellulose acetate. The calculated crystallinity index of the extracted cellulose was 73.725, and that of the prepared cellulose acetate was 36.853. The peak at about 8^0 is the main characteristic peak of semicrystalline cellulose acetate. This peak shows a disorder caused by the projection of the acetyl groups along the axis resulting in an increase in the interfibrillar distance and the destruction of the microfibrillar structures [10]. In addition, the bigger acetyl groups replacing the hydroxyl groups destroyed the cellulose intra- and intermolecular hydrogen bonding and consequently, reduces the crystallinity of acetylated cellulose [27].

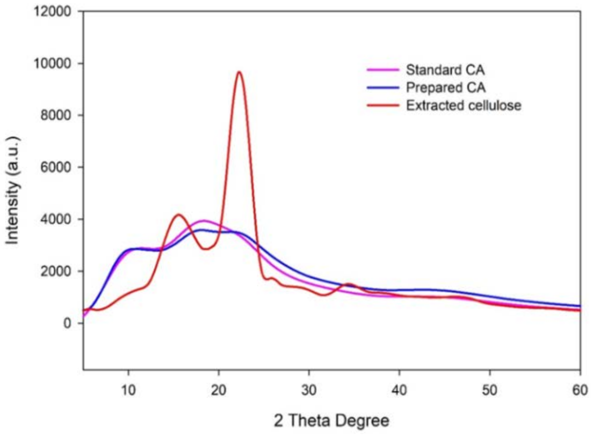

Figure 7. XRD chromatograms for the extracted cellulose, the prepared CA, and the standard CA

3.4. Thermogravimetric Analysis

The thermogravimetric analysis of the prepared CA and standard CA showed similar degradation trends in the whole temperature range as observed in Figure 8(a). In the TGA curves, the T onset (T_O) is used to determine the thermal stability of materials because it is known to have the highest repeatability [28]. The T_O values for the extracted cellulose, the prepared CA, and the standard CA are 301.4°C, 329.84°C, and 356.56°C respectively. An increase in thermal degradation temperature indicated an increase in cellulose thermal stability after acetylation. Marked decomposition of cellulose acetate occurred between 325°C and 400°C, with a sample loss of 70 % for the prepared CA and 78% for the standard CA. This results from the degradation of the cellulose backbone of the polymer. The observation is characteristic of the thermal degradation of cellulose acetate [27]. Finally, the charred residue was obtained at 625°C as 14.14 %, 12.98 %, and 12.43 % for the cellulose, prepared CA, and standard CA respectively.

From the differential thermogravimetric curves in Figure 8(b), the large exothermic peaks of both samples of cellulose acetate as well as cellulose near 400°C are a result of degradation of the natural cellulose structure [27]. The temperature of the maximum weight loss for the standard CA was 384.06°C and the prepared CA was 377.93°C, which was higher than that of extracted cellulose (373.2°C). This observation was consistent with the research of Huang et al. (2014) on the acetylation of rice straw fibers [25]. The increase in cellulose acetate's stability is associated with forming a newly organized structure compared to that of unsubstituted cellulose.

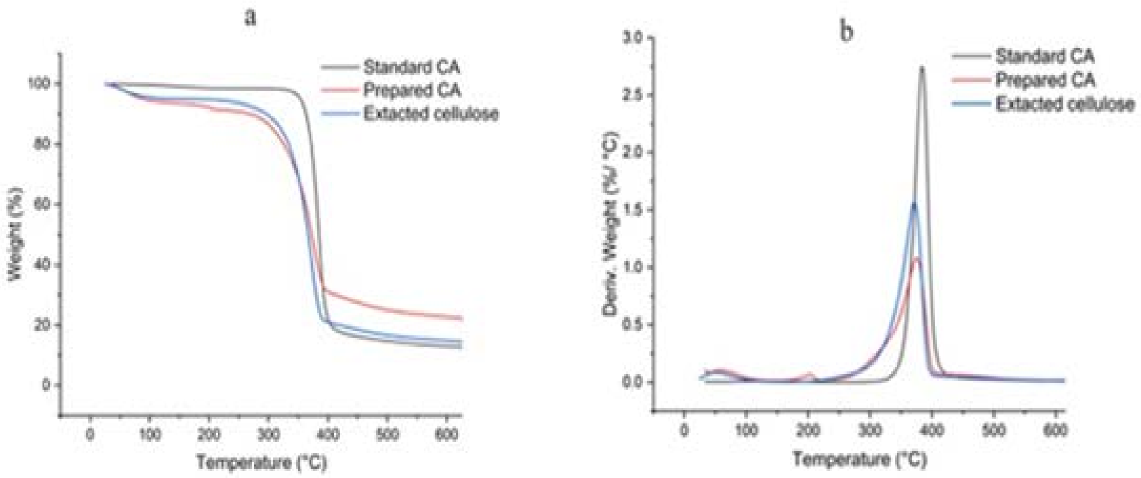

Figure 8. TGA (a) and DTG (b) thermograms for extracted cellulose, prepared CA, and standard CA

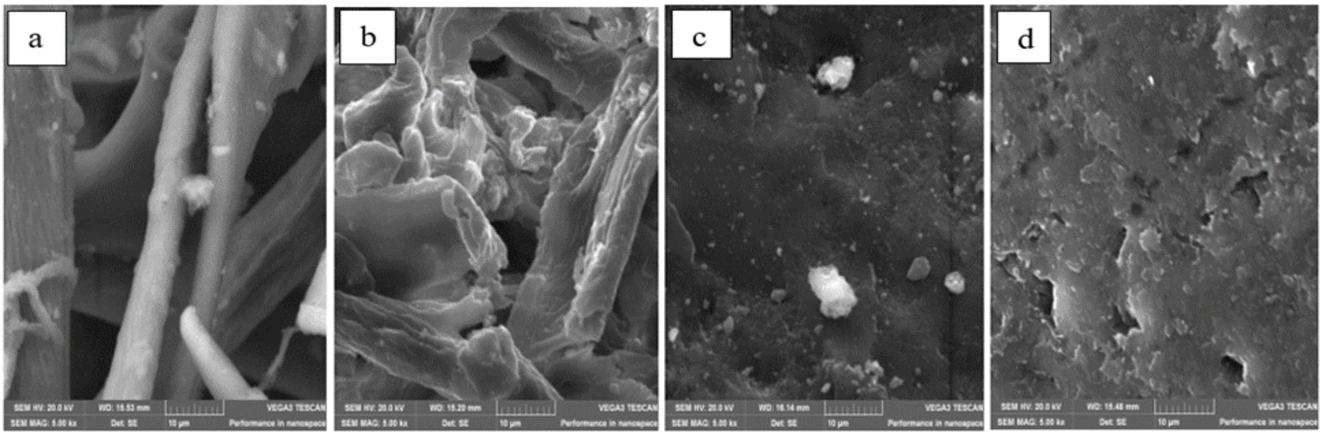

Figure 9. SEM micrographs (magnification 5.00 kx) for **(**a) raw sample, (b) extracted cellulose, (c) prepared cellulose acetate, and (d) standard cellulose acetate

3.5. Morphological Analysis by Scanning Electron Microscopy (SEM)

The SEM micrographs of the raw material, the extracted cellulose, the prepared cellulose acetate, and the standard are displayed in Figure 9. In the raw sample, the cellulose fibers appear to have a smooth, undamaged surface as shown in Figure 9(a). This is due to the binding of the fibers in the semi-epidermal layer of the leaves.

Figure 9(b) shows the SEM micrograph of extracted cellulose. The alkaline and bleaching treatments resulted in high-quality cellulose with a regular-like structure due to the aligning of the several microfibrils of cellulose. The fiber strands are arranged in an uneven network arrangement and have a ribbon-like pattern. Ma'ruf et al. (2023), and Egot and Alguno (2018) noted a similar observation about the cellulose derived from rice husks and pineapple leaves respectively [11,21].

This characteristic of the structure of the pure fiber is suitable for the swelling ability of cellulose and effective acetylation [21]. The cellulose acetate sample in Figure 9(c) shows a rough surface with loose particles in clusters of different sizes indicating changes in the crystal structure. This is almost similar to standard cellulose acetate in Figure 9(d). The rough surface of CA is suitable as it provides more contact points and hence improves the mechanical properties of the material in composite formation [29]. This observation is consistent with the characteristic results of XRD and FTIR analysis hence confirming the effective acetylation of cellulose. The structure disruption of cellulose allows for more free energy for reaction making cellulose acetate soluble in organic solvents unlike cellulose [30].

4. Conclusion

An optimized acetylation process was developed for cellulose acetate preparation. The effectiveness of acetylation mainly depended on catalyst loading and reaction time at a constant ratio of cellulose, glacial acetic acid, and acetic anhydride of 2:35:10 respectively. The achieved optimum results were 48.85% WPG, PAC of 43.26 %, and DS of 2.822. The variance between the actual and anticipated results was within reasonable limits, hence the findings validated the appropriateness and accuracy of the model. Following the chemical treatment, the cellulose X-ray diffraction patterns changed, as shown by the strong crystalline peak at position 22 (2ϴTheta) becoming less prominent suggesting a reduced level of crystallinity in comparison to cellulose. The characteristic ester carbonyl (C=O) and (C-O) absorption peaks in the O-C=O group and their enhanced relative intensity verified ester bond formation in the acetylated cellulose in FTIR analysis. The SEM micrographs obtained were characteristic of those observed in the reference standard cellulose acetate. The TGA and DTG analysis data indicated an increase in the thermal stability of acetylated cellulose in comparison with the native cellulose. The obtained results confirmed the effective synthesis of cellulose acetate, which is needed for the production of sustainable biodegradable polymers.

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Declaration Interests Statement

There was no conflict of interest disclosed by the authors.

List of Abbreviations

RSM = Response surface methodology
WPG = Weight percent gain
PAC = Percent acetyl content
DS = Degree of substitution
TGA = Thermal gravimetric analysis
XRD = X-ray diffraction
FTIR = Fourier transform infrared
SEM = Scanning electron microscopy
CA = Cellulose acetate
CMA = Cellulose monoacetate
CDA = Cellulose diacetate
CTA = Cellulose triacetate

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