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Preparation and Characterization of Acetate Cellulose Laurate Ester in Sodium Acetate/Zinc Chloride Systems

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Abstract
The objective of this study was to explore the preparation and characterization of acetate cellulose laurate ester in sodium acetate/zinc chloride systems. The cellulose used in the study was obtained from oil palm empty fruit bunch and oil palm frond. The characterization of both the isolated cellulose and the acetate cellulose laurate ester was carried out using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Differential thermogravimetric (DTG), and Thermogravimetric analysis (TGA). The FTIR analysis of the acetate cellulose laurate ester revealed the presence of C=O, confirming its modification. The crystallinity of the isolated cellulose and the acetate cellulose laurate ester was found to be 67–72% and 51–54%, respectively. The thermal stability of isolated cellulose and modified cellulose esters as revealed by TGA-DTG was 360–340 °C and 380–365 °C, respectively. The solubility test showed that the prepared acetate cellulose laurate esters were soluble in different solvents. However, this study found that the synthesis of acetate cellulose laurate ester in an aqueous medium is not feasible. The improved hydrophobic character, good thermal stability, water retention value, and excellent solubility in different solvents of the acetate cellulose laurate ester reported in this study make it a potential material for applications in bioplastics, and packaging materials.

Keywords:
Cellulose; solubility; thermal stability; hydrophobicity; modification; crystallinity; water retention value

1. Introduction

Cellulose is a renewable natural polymer material that can be found in all plants, including oil palm waste like oil palm empty fruit bunches and oil palm fronds [1]. The oil palm is a tropical plant that thrives in warm climates at elevations below 500 meters above sea level and requires at least 1.5 meters of spacing above ground level [2]. Oil palm empty fruit bunches are devoid of fruits, while palm fronds contain oil palm leaves [3]. Studies have shown that oil palm empty fruit bunches (OPEFB) and oil palm fronds (OPF) are lignocellulosic sources that can be used as raw materials for cellulose production [4].

Cellulose and its derivatives, such as cellulose esters, are used in numerous industries to produce cellulose-related products like foods, plastics, films, and pharmaceutical products [5]. Cellulose is a linear and semi-crystalline polysaccharide that consists of repeating anhydroglucose units (AGUs) linked by β-1,4-glycosidic bonds [6,7]. As the campaign against environmental degradation continues, cellulose has been identified as an alternative to petroleum, and its use for producing many new

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materials has increased geometrically due to its economic merits such as abundance, biodegradability, low cost, sustainability, renewability, nontoxicity, ease of modification, and biocompatibility [8]. Despite these advantages, cellulose cannot be used directly for many applications due to some drawbacks, such as insolubility in water and some organic solvents. This is primarily due to the intra- and inter-molecular hydrogen bonds within its polymer structure. Additionally, the poor thermal plasticity of unmodified cellulose makes it unsuitable for compression moulding applications [8]. However, physical and chemical modification methods such as esterification and etherification can be used to alter the physicochemical properties of cellulose significantly [8].

Cellulose esters with long-chain residues of fatty acid chlorides are potential materials for bio-plastic applications due to their mechanical properties [9,10]. Previous studies have reported on the preparation of cellulose laurate ester through esterification using lauric acid as the esterifying agent [11–13]. Recently, Xiaoxiang et al. [14] reported the synthesis of cellulose laurate by transesterification in an AmimCl/DMSO cosolvent system and 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) as a catalyst using vinyl laurate as an acylation agent. Schenzel et al. [15] have also reported the synthesis of cellulose laurate through the transesterification method using 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) as a catalyst. Long-chain cellulose esters have been prepared by many researchers, but the negative impact of the spent reagents on the environment and the high cost of the reagents used have been noted [16–21]. The introduction of acetate groups, in addition to the laurate groups, onto the cellulose chain can potentially enhance the physicochemical properties of cellulose derivatives products [16,22]. This necessitates the need for an environmentally friendly and cost-effective method for preparing acetate cellulose laurate ester.

Therefore, this study presents a simple method of preparing acetate cellulose laurate ester using a sodium acetate/zinc chloride system. Sodium acetate/zinc chloride system has low toxicity and requires no acid scavengers. Moreover, this study successfully demonstrated the extraction of cellulose from oil palm waste using this method.

2. Materials and Methods

2.1. Materials

The chemical reagents used are sodium hydroxide (>99%), anhydrous sodium sulphite (>97% purity), nitric acid (70% purity), hydrochloric acid (36% purity), potassium hydroxide (>98% pure), ethanol and methanol (99% purity), lauroyl chloride (>98% purity), sodium hypochlorite 3.5% *w*/*v*, sulphuric acid (98% purity), anhydrous zinc chloride (AR, Kermel, 98%), toluene (>98%). All the reagents are purchased from Sigma-Aldrich and AR Karmel and used as purchased.

The cellulose used in this study was extracted from oil palm empty fruit bunch (OPEFB) and oil palm frond (OPF) according to a method described in our previous studies (see supplementary section) [2,4]. The proximate analysis of the OPEFB and OPF has also been reported in the previous studies [2,4]. The isolated cellulose from oil palm empty fruit bunch and oil palm frond were denoted ICB, and ICF, respectively.

2.2. Methods

2.2.1. Preparation of Acetate Cellulose Laurate Ester in an Aqueous Medium

To gain insight into the behaviour of cellulose-lauroyl chloride in water, lauroylation in an aqueous environment was performed based on the method outlined in our previous studies [2,4] with minor adjustments. The activation of ICB or ICF (1.0 g) was initiated by NaOH (20 mL; 0.5 M) in a 500 mL beaker. The cellulose-NaOH mixture was mechanically stirred at 300 rpm for 10 minutes at 30 ± 2 °C using a KJJ-1 fixed-time power mixer (model KJJ-1 60 W). Lauroyl chloride (5 mL) was added gradually to the activated cellulose using a burette while continuous stirring was maintained on a magnetic stirrer (model hotplate 78-1) at 30 ± 2 °C. The solution was maintained in an alkaline region by carefully adding NaOH (0.5M). The product was filtered and washed with ethanol (15 mL) three times, followed by distilled water three times. The product was further washed with ethanol three times and acetone three times and dried at 50 °C for 48 h using a thermostat oven (model DHG-9101-OSA). ICF was treated similarly.

2.2.2. Preparation of Acetate Cellulose Laurate Ester in Sodium Acetate/Zinc Chloride Medium

To initiate the activation process of cellulose, 20 mL of sodium acetate (1 M) was added to ICB (1.0 g) in a pre-dried round flat-bottom flask (model DHG-9101-OSA) at 60 °C for 8 h using a hotplate stirrer (model hotplate 78-1) at 250 rpm. The mixture was stirred at 30 ± 2 °C for 20 minutes, after which anhydrous zinc chloride (1 wt%) was added and stirred for 15 minutes at 50 °C. Subsequently, lauroyl chloride (5 mL) was slowly added to the activated cellulose mixture using a burette while continuously stirring. Once all the lauroyl chloride was added, the solution was refluxed at 90 °C for 45 minutes. The mixture was then poured into 50 mL of ethanol to precipitate

2024, Vol. 1, Article ID. 2024.0003
www.doi.org/10.69709/BIOMATC.2024.171176

the acetate cellulose laurate ester. The precipitated product was filtered using vacuum filtration and washed with ethanol (15 mL) three times and acetone (30 mL) five times. The acetate cellulose laurate ester (ACLB-5) was dried at 60 °C for 24 h using the aforementioned drying equipment. Further, the process was repeated with ICF to obtain ACLF-5.

2.2.3. Determination of Degree of Substitution of Acetate Cellulose Laurate Ester

To determine the degree of substitution (DS) of the acetate cellulose laurate ester, the titrimetric method described by Lawal et al. [23] with minor modifications was employed. One gram of each sample (ACLB-5 or ACLF-5) that had been dried at 60 °C for 24 h was dissolved in 1% aqueous sodium chloride and titrated with NaOH (1 M) using a phenolphthalein indicator. The titration was stopped when the phenolphthalein indicator's color permanently disappeared, indicating the endpoint. The DS was calculated using the following Equation (1)

$$DS = \frac{nNaOH \times m_c}{w_c - nNaOH \times m_l} \quad (1)$$

where m_c is the molar mass of the anhydroglucose unit (162 g/mol), m_l is the molar mass of lauroyl residue (g/mol), n NaOH is the amount of sodium hydroxide used (mol), w_c is the corrected weight of modified cellulose (g).

The corrected weight of modified cellulose (w_c) is given by Equation (2).

$$w_c = \frac{m_c \times (m_c \times t)}{100} \quad (2)$$

w_c is the modified cellulose weight (g) and t is the moisture content.

2.2.4. Proximate Analysis of Isolated Cellulose and Acetate Cellulose Laurate Ester

Proximate analysis (moisture, ash, crude fibre, and crude fat contents) of isolated cellulose (ICB, ICF) and acetate cellulose laurate ester (ACLB-5 and ACLF-5) was determined according to standard AOAC methods (AOAC, 1996) without modification.

3. Characterization of Isolated Cellulose and Acetate Cellulose Laurate Ester

3.1. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared (FTIR) spectra of isolated cellulose and acetate cellulose laurate ester were recorded by a PerkinElmer Spectrum 100 (PerkinElmer, Waltham, MA, USA) using the KBr pellet procedure for both samples. Before the measurement, the KBr tablets were dried at 105 °C for 3 h to get rid of moisture.

3.2. Crystallinity

The crystallinity of the native cellulose and acetate cellulose laurate ester was investigated by a D-8 Advance instrument operated at 40 mA and voltage 45 kV at 25 °C with Cu Kα. The measurement was recorded at an angle 2θ value between 5 to 50° at a scan speed of 3.00°/min.

3.3. Thermal Stability

The thermal stability of both samples was characterized by using TGA/DTG on a QG500 thermogravimetric analyzer. About 2–3 mg of samples were heated from 20 to 800 °C under a nitrogen atmosphere at a heating rate of 10 °C/min.

3.4. Water Retention Value Measurement

Water retention value (WRV) is an important method of evaluating the hydrophobic behaviour of cellulosic materials relative to moisture absorption. The water retention value was determined according to the method reported in our previous studies [2,4].

4. Results and Discussions

4.1. Preparation of Acetate Cellulose Laurate Ester in an Aqueous Medium

The preparation of acetate cellulose laurate ester in an aqueous medium provided valuable information about the behaviour of native cellulose in long-chain fatty acid chlorides. Specifically, it was observed that lauroyl chloride was decomposed into its corresponding carboxylic acid by water molecules, leading to the rupture of the fibrillar architecture of cellulose during activation with sodium hydroxide, lauroyl chloride, and its corresponding carboxylic acid. This resulted in the absorption of the compounds into the cellulose matrix, causing excessive swelling. It suggests that acid hydrolysis occurs between lauroyl chloride and sodium hydroxide, which is detrimental to the esterification reaction. When the reaction temperature exceeded 40 °C, cellulose degradation occurred, leading to browning, which is consistent with previous findings by Jérôme et al. [24]. Therefore, the preparation of acetate cellulose laurate ester in an aqueous medium is not feasible. The flowchart of the extraction of cellu-

lose from oil palm waste, as previously reported in our studies, is shown in Figure S1. It has been previously reported that modifying cellulose with long-chain fatty acids in NaOH/ethanol solution as non-acidic catalysts at high temperatures is not effective [24]. This study suggests that a lauroyl chloride-water-NaOH cosolvent would be an appropriate solvent for achieving the maximum swelling of cellulose. Scheme 1 illustrates the mechanism of this reaction.

4.2. Preparation of Acetate Cellulose Laurate Ester in Sodium Acetate/Zinc Chloride Medium

The cellulose, whether it be ICB or ICF, was activated by sodium acetate. The mixture's pH was stabilized by the formation of acetic acid and the presence of unreacted sodium acetate, which acted as a buffer. The addition of zinc chloride and the reaction medium increased the nucleophilic properties of the cellulose surface and the electrophilic character of the alpha carbon atom of lauroyl chloride, respectively. Under these conditions, lauroyl chloride underwent a substitution reaction at the expense of hydrolysis. The reaction between $ZnCl_2$ and sodium acetate resulted in the formation of an acetyl group, which reacted with the cellulose-hydroxyl groups available through nucleophilic attack during esterification [16,17].

The reaction mechanism of cellulose with lauroyl chloride in a sodium acetate/zinc chloride system is depicted in Scheme 2. This method was more effective and saved time and energy compared to traditional methods like DMSO, pyridine, LiCl/DMAc solvents, etc., in which the extent of modification could be limited by an increase in precipitation of the modified product [25]. The test for the acetyl group was positive, indicating its presence in the modified cellulose structure. The modification of cellulose with lauroyl chloride in trifluoroacetic anhydride [13], 1-Allyl-3-methylimidazolium chloride (AmimCl)/DMSO [14], LiCl/DMAc, and pyridine [26] has been reported. To ensure effective modification, as demonstrated in this study, all apparatus must be thoroughly dried, free of moisture, and lauroyl chloride should be added dropwise. The cellulose particles should be powdery for effective collision between the cellulose surface-hydroxyl groups and lauroyl chloride.

4.3. Proximate Analysis of Isolated Cellulose and Acetate Cellulose Laurate Esters

The outcome of the proximate analysis of isolated cellulose (ICB and ICF) and acetate cellulose laurate ester (ACLB-5 and ACLF-5) is depicted in Table 1. The findings revealed that the moisture content of the acetate cellulose laurate esters was lower than that of unmodified cellulose, which may be attributed to the increased hydrophobic character of acetate cellulose laurate ester compared to its native form. Additionally, the observed decrease in the percentage ash content of acetate cellulose laurate ester relative to unmodified cellulose might be due to the loss or erosion of the mineral content inherent in the cellulose during modification. Similarly, the reduction in ash content of ACLB-5 ($1.62 \pm 0.02\%$) and ACLF-5 ($1.71 \pm 0.03\%$), as well as the decrease in fiber and fat contents of ACLB-5 and ACLF-5 compared to isolated cellulose (ICB and ICF), was attributed to the effect of slight degradation resulting from the esterification process.

4.4. Effect of Preparation Method on the Degree of Substitution

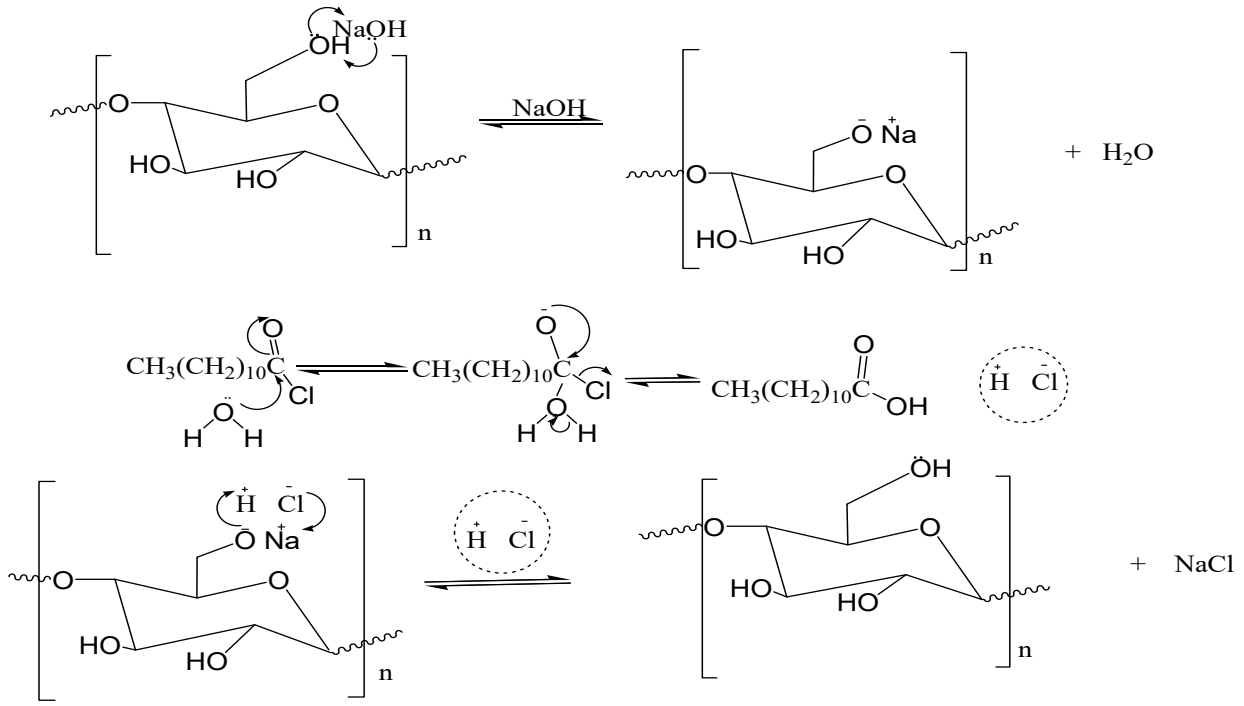
The degree of substitution was determined using Equation (1), which showed that ACLF-5 and ACLB-5 had average degrees of substitution of 0.6 and 0.9, respectively. As the reaction time and molar ratio of AGU to lauroyl chloride was increased while keeping other reaction conditions constant, the degree of substitution also increased. Willberg-Keyrilainen and Jarmo previously reported a DS of 0.9 for cellulose laurate ester made using a homogeneous method in LiCl/DMAc solution and pyridine at 80 °C for 16 h or 100 °C for 5 h [26]. Xiaoxiang et al. also found that the DS of cellulose laurate ester increased from 1.47 to 2.41 with higher reaction temperatures (70–120 °C) and reached 2.63 with a molar ratio of 1:12 [14]. Willberg-Keyrilainen and Jarmo also reported that the DS of homogeneously esterified cellulose ester increased from 0.3 to 1.3 depending on the length of the side chain [26]. Schenzel et al. reported a DS value of 0.4 for long-chain cellulose esters made using 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) as a catalyst at 115 °C for 24 h [15]. The use of zinc chloride shielded the hydroxyl groups from the bulkiness of lauroyl chloride, which increased electron density and promoted effective interaction with the alpha carbon atom of lauroyl chloride, leading to a steadily increased DS value.

5. Characterization

5.1. Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectra of acetate cellulose laurate ester and isolated cellulose are depicted in Figure 1. The peak observed in the range of 3250–3600 cm^{-1} was assigned to

2024, Vol. 1, Article ID. 2024.0003
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Scheme 1: Mechanism for the Reaction of Cellulose with Lauroyl Chloride in Aqueous Medium.

Table 1: Proximate analysis of isolated cellulose and acetate cellulose laurate ester.

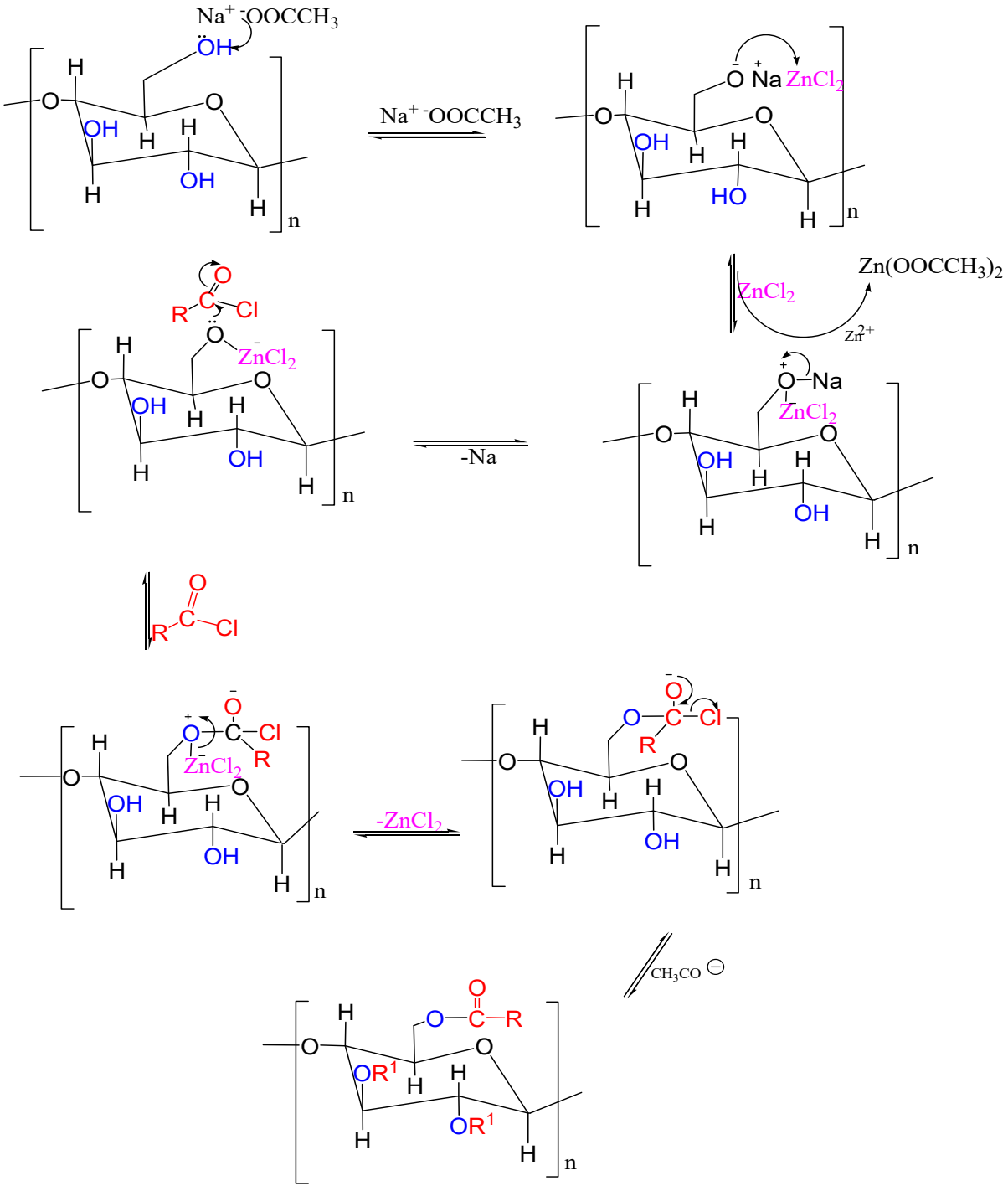
Samples	Moisture Content (%)	Ash Content (%)	Crude Fibre (%)	Crude Fat (%)
ICB	6.06 ± 0.27	2.0 ± 0.16	6.96 ± 0.10	0.89 ± 0.02
ICF	5.82 ± 0.13	3.04 ± 0.02	7.01 ± 0.03	0.68 ± 0.05
ACLB-5	3.85 ± 0.03	1.62 ± 0.02	3.14 ± 0.03	0.32 ± 0.04
ACLF-5	3.81 ± 0.01	1.71 ± 0.03	3.51 ± 0.02	0.29 ± 0.01

vO–H stretching vibration resulting from hydrogen bonding [4]. The peak in the range of 2950–2800 cm^{-1} was identified as C–H (methyl; asymmetry), while the absorption peaks at 1614 cm^{-1} and 1655 cm^{-1} in the ICB and ICF spectra, respectively, were attributed to water molecules inherent in the cellulose fiber capillary. Additionally, the peak in the range of 1420–1376 cm^{-1} was assigned to CH_2 bending vibration. The weak peaks in the range of 1250–1130 cm^{-1} and at 1050 cm^{-1} in all the samples may be attributed to δCH_2 and C–O–C asymmetric stretch vibration, respectively [27]. The noticeable peaks with a weak pointed shoulder in the range of 950–860 cm^{-1} in all the samples were attributed to C1–O–C of β-(1–4)-glycosidic linkages stretching vibration in cellulose I. The appearance of the peak in the range of 1720–1740 cm^{-1} in acetate cellulose laurate esters (ACLB-5 and ACLF-5) spectra was attributed to C=O ester stretching, revealing the preparation of ACLB-5 and ACLF-5. The absence of an absorption peak at 1800 cm^{-1} in the spectra indicated that the products are free of any unreacted acid chloride.

5.2. X-Ray Diffraction (XRD)

The X-ray diffraction (XRD) patterns of acetate cellulose laurate ester and unmodified cellulose are shown in Figure 2. The Scherrer crystallite size of ICB and ACLB-5 were 1.654 ± 0.0399 nm and 0.978 ± 0.0526 nm, and ICF and ACLF-5 were 1.179 ± 0.0313 nm, and 0.948 ± 0.0463 nm, respectively. These values are the average crystal dimensions of the cellulose particles. The crystallinity index of ICB, ACLB-5, ICF, and ACLF-5 were 67.22%, 51.66%, 72.18%, and 54.07%, respectively.

In this study, the isolated cellulose from oil palm waste was found to have a highly crystalline structure, which is attributed to inter- and intra-molecular hydrogen bonds. This finding is consistent with previous lit-



Scheme 2: Mechanism of Reaction of Cellulose with Lauroyl Chloride in Sodium Acetate/Zinc Chloride Medium.

2024, Vol. 1, Article ID. 2024.0003
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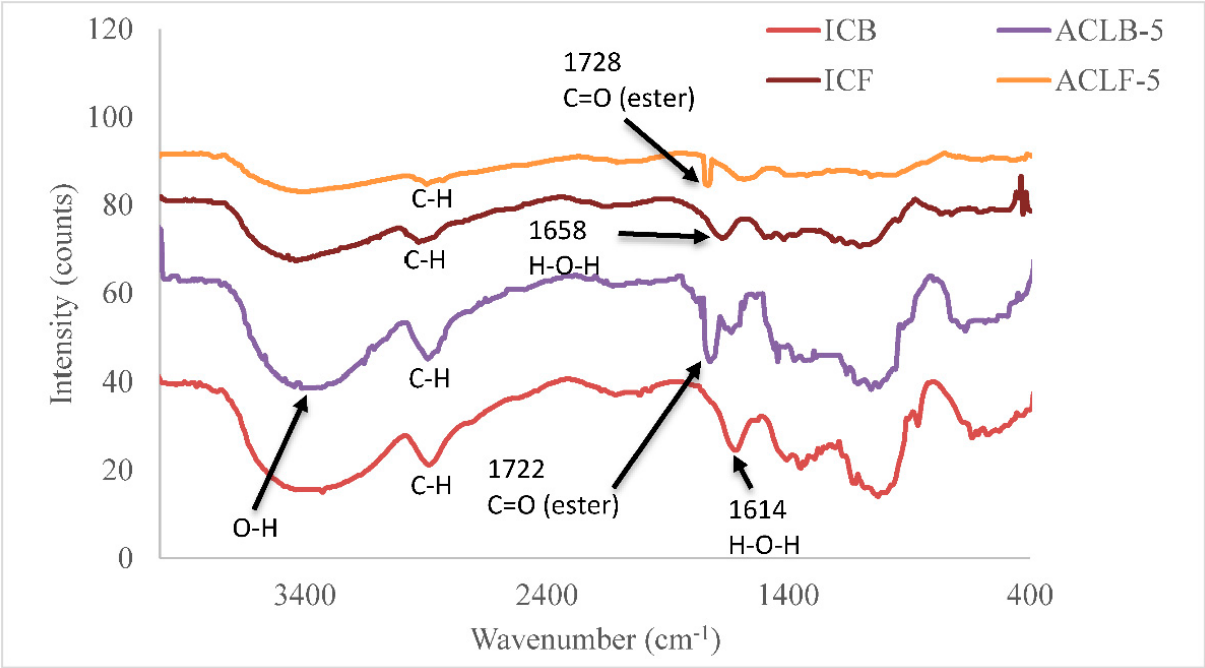


Figure 1: FTIR of Isolated Cellulose (ICB and ICF) and Acetate Cellulose Laurate Ester (ACLB-5 and ACLF-5).

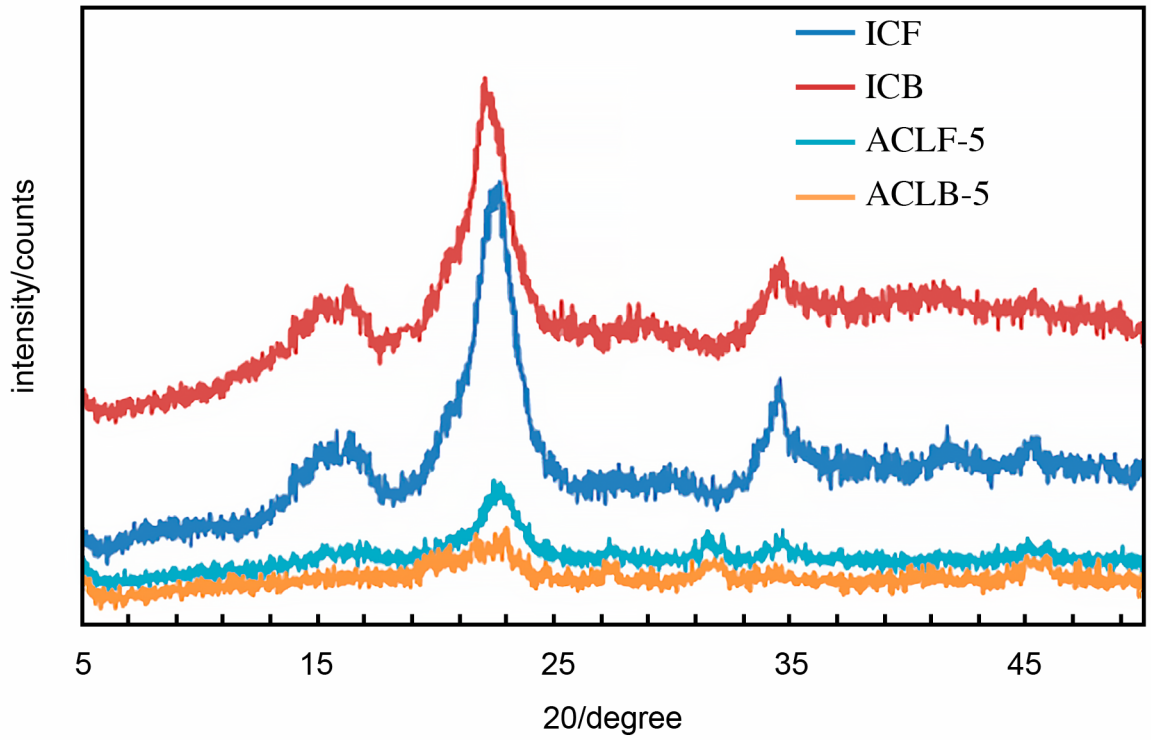


Figure 2: X-ray diffractograms of Isolated Cellulose and Acetate Cellulose Laurate Esters.

erature. [28,29]. In comparison, the low crystallinity of acetate cellulose laurate esters (52.86%) compared to cellulose benzoate ester (61.38%) prepared in an aqueous medium, as reported in our previous studies [2,4], may be attributed to an increased amorphous character resulting from the introduction of an acetate group into the cellulose backbone, which accounts for the broadness of ACLB-5 and ACLF-5 diffractogram peak at 2θ = 21–24° [14].

5.3. Thermogravimetric Analysis

The thermal stability of both isolated cellulose and acetate cellulose laurate esters was investigated using TGA and DTG, and the thermogram curves are shown in Figure 3. As can be seen from the curves, both isolated cellulose and acetate cellulose laurate esters (ACLB-5 and ACLF-5) had initial weight loss (2–8 wt%) below 140 °C, which was due to the evaporation of water inherent in cellulose fiber capillaries. The second step of ICB and ICF decomposition began at 240 °C and 220 °C, respectively, and terminated at 360 °C and 340 °C, respectively. For ACLB-5 and ACLF-5, the second step of decomposition started at 290 °C and 280 °C, respectively, and ended at 380 °C and 360 °C, respectively. The increased thermal stability of ACLB-5 and ACLF-5 confirms the formation of acetate cellulose laurate esters. The introduced long-chain fatty acid group onto the cellulose skeleton might be orderly arranged to form a new ordered structure, which could be accountable for the enhanced thermal stability [9,30]. Additionally, the increased amorphous character could be attributed to the presence of acetyl groups formed through esterification, as indicated by the XRD analysis. The cellulose degradation occurred via dehydration, depolymerization, and glucosan formation, leading to the cleavage of 1,4 glycosidic bonds [31]. The pyrolysis residues (char) at 800 °C were likely due to a high carbon content from the bonded acetyl group and lauroyl chloride [32].

The Differential Thermogravimetric (DTG) curves indicated that the degradation of ACLB-5 and ACLF-5 occurred at regions 380 °C and 365 °C, respectively, with the evolution of volatile products [33], which supported the TGA result. The degree of heat intensity associated with the acetate cellulose laurate esters, as shown by the DTG (Figure 4), could be due to the cumulative effect of acetyl groups and long-chain hydrocarbon residues.

5.4. Hydrophobicity

To test the extent of hydrophobicity and hydrophilicity of the acetate cellulose laurate ester and unmodified cellulose, respectively, water retention value (WRV) was used. Water retention value gives information on the penetration of water into the interior parts of the cellulose fibers via the capillary system. The WRV of ICB and ICF decreased from 128 ± 1.009% to 113 ± 1.018% and 125 ± 1.672% to 110 ± 0.948%, respectively, as reported in our previous studies [2,4]. The high WRV of ICB and ICF was due to their hydrophilic properties. The WRV of ACLB-5 and ACLF-5 were 52 ± 1.046% and 55 ± 1.004%, respectively. The low WRV of ACLB-5 and ACLF-5 signified a high degree of hydrophobization, which agreed with other analysis. The long aliphatic chains are hydrophobic while cellulose is hydrophilic. Thus, the higher the aliphatic side chains attached to the cellulose backbone or chain, the higher the hydrophobicity of the modified cellulose. It was noted that variables such as surface area, weight of samples, and particle size do not significantly affect the WRV, which agreed with [4,34].

5.5. Solubility

The study investigated the solubility of acetate cellulose laurate ester in various solvents. Most of the previously prepared cellulose laurate esters were found to be completely insoluble in tetrahydrofuran (THF), DMSO, and N-Dimethyformamide (DMF). However, the acetate cellulose laurate esters obtained in this study were found to be completely soluble in chloroform, partially soluble in THF, DMSO, and DMF, and completely insoluble in acetone, ethanol, and methanol. The extent of solubility may depend on the degree of substitution (DS). The findings suggest that the solubility of acetate cellulose laurate ester in THF, DMSO, and DMF enhances its industrial potential for the production of numerous cellulosic-based products such as films, tissue engineering, bioplastics, and packaging materials.

6. Conclusion

In conclusion, a novel method of introducing both acetyl group and long-chain fatty acid onto cellulose polymer chain simultaneously was explored. The study also examined the effect of the reaction medium and solubility. The results revealed that the sodium acetate/zinc chloride system is an excellent method of introducing both acetyl and long-chain fatty acid groups onto the cellulose backbone simultaneously. The benefits of this system include a short reaction time, ease of separation, and reduced environmental degradation caused by co-solvents. The improved hydrophobic character, high thermal stability, moderate water retention value, and excellent solubility in various solvents indicate that acetate cellulose laurate ester is a promising material for bioplastics, packaging, food, drug delivery, and pharmaceutical applications.

2024, Vol. 1, Article ID. 2024.0003
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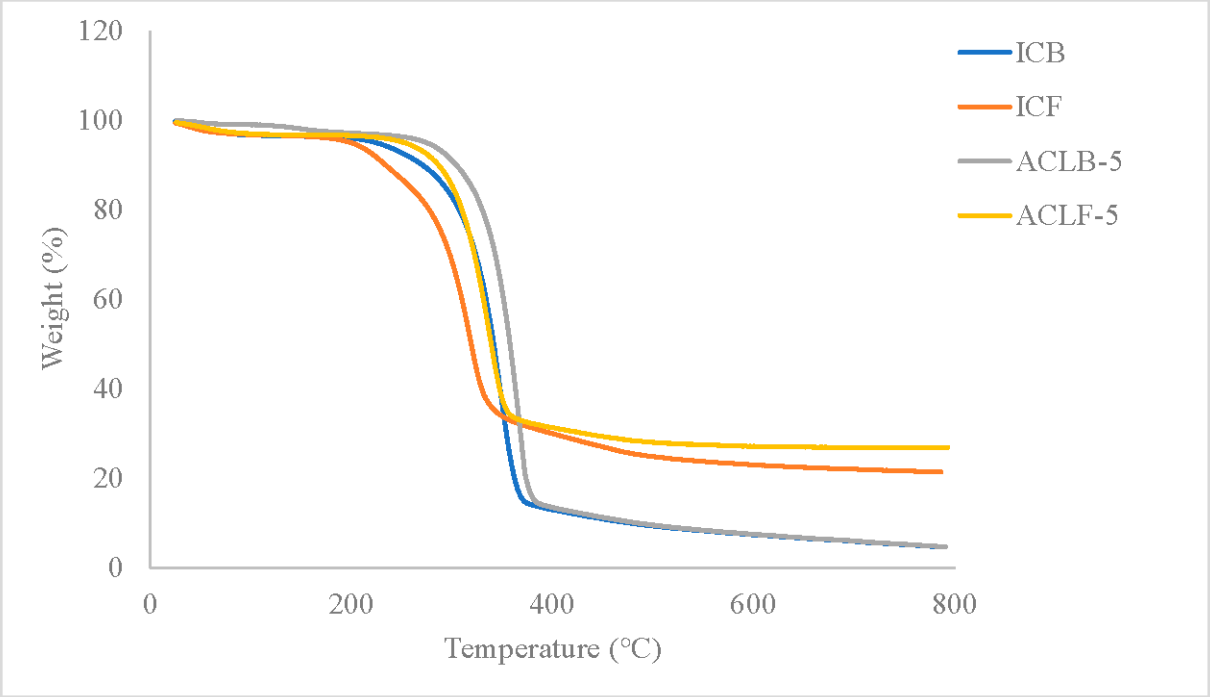


Figure 3: Thermogravimetric analysis (TGA) Curve of Isolated Cellulose and Acetate Cellulose Laurate Esters.

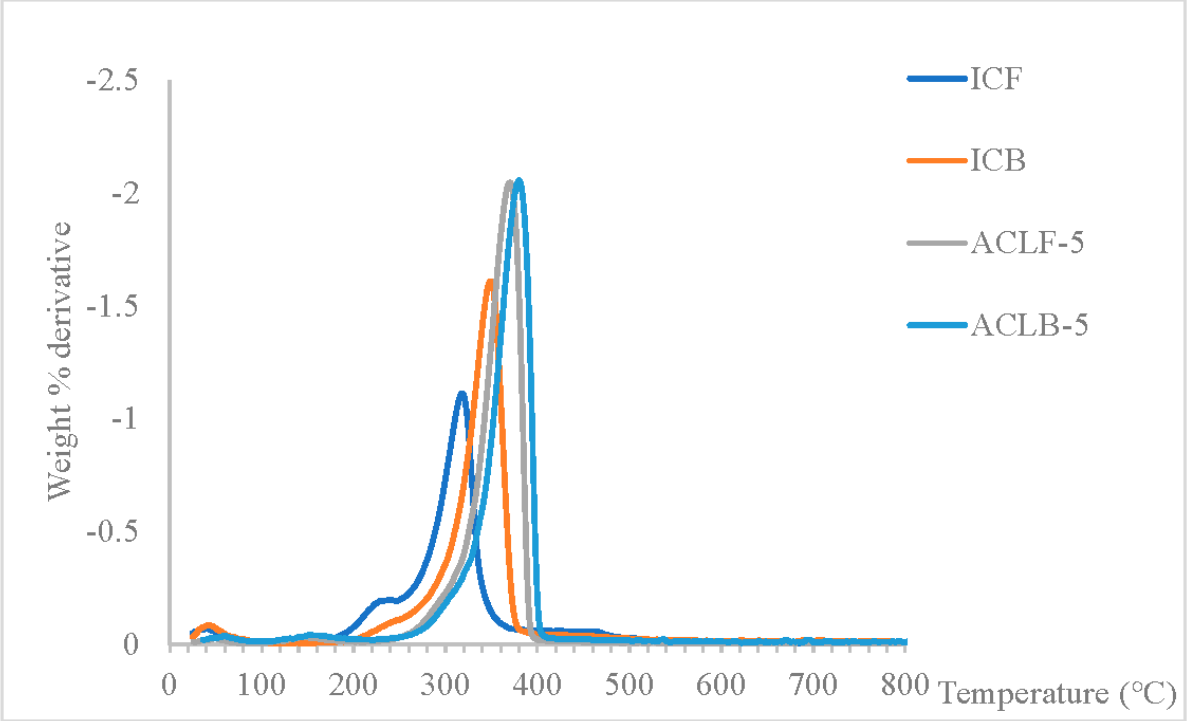


Figure 4: Differential Thermogravimetric (DTG) of Isolated Cellulose and Acetate Cellulose Laurate Esters.

List of Abbreviations

ACLB-5	Acetate cellulose laurate ester from oil palm bunch
ACLF-5	Acetate cellulose laurate ester from oil palm frond
AGU	anhydroglucose units
AOAC	Association of Official Analytical Chemists
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DMAc	Dimethylacetamide
DMF	N-Dimethyformamide
DMSO	Dimethylsulfoxide
DS	degree of substitution
DTG	Differential Thermogravimetric
FTIR	Fourier transform infrared spectroscopy
ICB	Isolated cellulose from oil palm empty fruit bunch
ICF	Isolated cellulose from oil palm frond
LiCl	lithium chloride
OPEFB	Oil Palm Empty Fruit Bunch
OPF	Oil Palm Frond
TBD	1,5,7-triazabicyclo [4.4.0] dec-5-ene
TGA	Thermogravimetric Analysis
THF	tetrahydrofuran
WRV	Water retention value
XRD	X-ray diffraction

Author Contributions

Conceptualization: S.O.O.; Methodology and investigation: S.M.A., S.O.O., A.E.D., M.O.A.; Formal analysis: S.M.A.; Validation: S.O.O., S.F.A., D.P.F., E.G.O., O.S.L., C.O.A.,: D.M.; Data analysis: S.F.A.; Resources: D.P.F.; Supervision: E.G.O., O.S.L., C.O.A., D.M.; Writing, original draft, visualization: S.M.A. All authors have read and agreed to the published version of the manuscript.

Availability of Data and Materials

All data and figures analyzed during this study are included in this article (or available in the cited references).

Consent for Publication

Not applicable.

Conflicts of Interest

The authors have no competing interests to declare that are relevant to the content of this article.

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AI Declaration

AI-based tools were used solely for language editing and formatting. No AI tool was used to generate the scientific content of the manuscript. The authors take full responsibility for the accuracy, originality, and integrity of the work.

Supplementary Materials

Download the Supplementary data to this article.

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