

**ALL CELLULOSE COMPOSITES  
PRODUCTIONS FROM OIL PALM EMPTY  
FRUIT BUNCHES**

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**ALL CELLULOSE COMPOSITES  
PRODUCTIONS FROM OIL PALM EMPTY  
FRUIT BUNCHES**

by

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## LIST OF SYMBOLS

%	Percentage
°C	Degree celcius
μm	Micrometer
C	Concentration
D	Dissolution time
g	Gram
GPa	Gigapascal
min	Minutes
ml	Milliliter
MPa	Megapascal
T	Temperature
t	Time
T <sub>g</sub>	Glass transition temperature
T <sub>m</sub>	Melting temperature
T <sub>max</sub>	Maximum temperature
v/v	Volume per volume
V <sub>f</sub>	Fibre volume fraction
Vol.	Volume
wt%	Weight percentage
Wt.	Weight

## LIST OF ABBREVIATIONS

ACC	All cellulose composite
Acetone	$(\text{CH}_3)_2\text{CO}$
Acid acetic	$\text{CH}_3\text{COOH}$
AmimCl	1-allyl-3-methylimidazolium chloride
APP	All-polypropylene composite
ASTM	American Society for Testing Materials
BL	Blank
BmimCl	Butyl-3-methylimidazolium chloride
C <sub>1</sub> D <sub>15</sub>	1% of initial cellulose concentration + 15-minute dissolution time
C <sub>1</sub> D <sub>30</sub>	1% of initial cellulose concentration + 30-minute dissolution time
C <sub>1</sub> D <sub>45</sub>	1% of initial cellulose concentration + 45-minute dissolution time
C <sub>1</sub> D <sub>5</sub>	1% of initial cellulose concentration + 5-minute dissolution time
C <sub>3</sub> D <sub>15</sub>	3% of initial cellulose concentration + 15-minute dissolution time
C <sub>3</sub> D <sub>30</sub>	3% of initial cellulose concentration + 30-minute dissolution time
C <sub>3</sub> D <sub>45</sub>	3% of initial cellulose concentration + 45-minute dissolution time
C <sub>3</sub> D <sub>5</sub>	3% of initial cellulose concentration + 5-minute dissolution time
C <sub>5</sub> D <sub>15</sub>	5% of initial cellulose concentration + 15-minute dissolution time
C <sub>5</sub> D <sub>30</sub>	5% of initial cellulose concentration + 30-minute dissolution time
C <sub>5</sub> D <sub>45</sub>	5% of initial cellulose concentration + 45-minute dissolution time
C <sub>5</sub> D <sub>5</sub>	5% of initial cellulose concentration + 5-minute dissolution time
$\text{CH}_3\text{COOH}$	Acid Acetic
CNCs	Cellulose nanocrystal
CrI	Crystallinity index

DMAc	N, N dimethylacetamide
DP	Degree of polymerization
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetry
EAB	Elongation at break
FFB	Fresh fruit bunch
FP	Filter paper
FTIR	Fourier transform infrared
HDPE	High density polyethylene
ILs	Ionic liquids
LCAs	Life cycle assessments
LiCl	Lithium chloride
MCC	Microcrystalline cellulose
MF	Mesocarp fiber
MFC	Microfibrillated cellulose
MPOB	Malaysian Palm Oil Board
NaClO <sub>2</sub>	Sodium chlorite
NaOH	Sodium Hydroxide
NMMO	N-methyl morpholine-N-oxide
NMR	Nuclear Magnetic Resonance
OH	Hydroxyl
OPEFB	Oil palm empty fruit bunch
OPF	Oil palm frond
OPT	Oil palm trunk
PEG	Poly (ethylene glycol)

PKS	Palm kernel shell
PLA	Polylactic acid
POME	Palm oil mill effluent
PP	Polypropylene composite
RH	Relative humidity
RSM	Response Surface Methodology
RT	Room temperature
SEM	Scanning electron microscopy
SPC	Single polymer composites
SPSS	Statistical Package for the Social Sciences
TA	Texture analyzer

## LIST OF APPENDICES

- Appendix A Certificate of silver medal on 6th International Innovation, Design and Articulation (i-IDeA 2023), UiTM Perlis
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# **PENGHASILAN KOMPOSIT SELULOSA SEPENUHNYA DARIPADA TANDAN SAWIT KOSONG**

## **ABSTRAK**

Kajian ini menyiasat formulasi dan sifat filem komposit selulosa sepenuhnya (ACC) daripada tandan sawit kosong (OPEFB) menggunakan pelarut 8% litium klorida/N-N dimetilasetamida (LiCl/DMAc) dan teknik pelarutan permukaan terpilih. OPEFB merupakan sumber boleh diperbaharui yang banyak tetapi kurang dimanfaatkan di Malaysia. Sebagai tindak balas kepada permintaan yang semakin meningkat untuk bahan berprestasi tinggi yang mampan, kajian ini meneliti kesan parameter keadaan pemprosesan terhadap ciri tegangan, struktur, terma, penyerapan air dan biodegradasi filem ACC. Pembuatan ACC melibatkan penggunaan formulasi parameter keadaan pemprosesan dengan masa pelarutan selama 5, 15, 30, dan 45 minit, yang digabungkan dengan kepekatan selulosa permulaan masing-masing sebanyak 1%, 3%, dan 5%. Teknik pemulpaan, pelunturan, dan penuangan larutan digunakan bagi mengekstrak pulpa selulosa OPEFB, memastikan pembuatan filem yang cekap. Analisis tegangan menunjukkan bahawa kombinasi terbaik ialah kepekatan selulosa awal 3% dan masa pelarutan 15 minit menghasilkan filem ACC dengan kekuatan tegangan tertinggi (44.41 MPa) dan modulus Young (3.26 GPa). Kajian pembelauan sinar-X (XRD) menunjukkan peralihan struktur selulosa yang larut dari selulosa I kepada selulosa II, mengesahkan kewujudan bersama fasa selulosa I dan selulosa II, mengakibatkan pengurangan ketara dalam darjah penghabluran yang diperhatikan dalam filem ACC. Analisis spektroskopi infra merah transformasi Fourier (FTIR) yang menggunakan indeks penghabluran keseluruhan (TCI) seterusnya menyokong hasil penilaian penghabluran yang dijalankan dengan XRD yang serupa.

Kajian termogravimetri menggunakan analisis termogravimetri (TGA) dan kalorimetri pengimbasan pembezaan (DSC) menunjukkan sedikit penurunan kestabilan terma dengan peningkatan masa pelarutan. Pemeriksaan suhu maksimum ( $T_{max}$ ) berhubung masa pelarutan menunjukkan penurunan  $T_{max}$  yang konsisten, disebabkan oleh peningkatan pemecahan ikatan hidrogen dan pengurangan darjah penghabluran. Penemuan XRD dan FTIR menunjukkan hubungan antara pengurangan darjah penghabluran dan penurunan kestabilan terma. Pemeriksaan menggunakan mikroskopi elektron pengimbasan (SEM) mengesahkan perubahan dalam mod kegagalan komposit filem dan peningkatan permukaan dengan pengurangan ruang kosong. Berdasarkan penemuan ini, kajian ini meneroka kesan masa pelarutan dan kepekatan selulosa permulaan terhadap sifat penyerapan air dan biodegradasi filem ACC. Penyerapan air menunjukkan interaksi kompleks antara masa pelarutan, kepekatan selulosa permulaan, dan sifat hidrofilik, dengan filem ACC memperlihatkan tingkah laku penyerapan air yang unik. Kajian biodegradasi menekankan peranan penting kepekatan selulosa permulaan dan masa pelarutan, dengan kedua-dua faktor mempengaruhi kadar degradasi secara semulajadi yang lebih perlahan. Kepekatan selulosa permulaan yang lebih tinggi memberi kesan kadar degradasi yang lebih perlahan. Penyelidikan menyeluruh terhadap pelbagai sifat filem ACC berasaskan OPEFB ini menghasilkan penemuan penting mengenai ciri-ciri tegangan, struktur, terma, penyerapan air, dan biodegradasi. Penemuan ini meningkatkan pemahaman terhadap reka bentuk bahan mampan dan menawarkan aplikasi yang pelbagai, menekankan keperluan untuk mengoptimumkan parameter pemprosesan untuk pembangunan komposit yang mesra alam.

# **ALL CELLULOSE COMPOSITES PRODUCTIONS FROM OIL PALM EMPTY FRUIT BUNCHES**

## **ABSTRACT**

This research study the formulation and properties of all cellulose composite (ACC) films isolated from oil palm empty fruit bunch (OPEFB) using 8% lithium chloride/N-N dimethylacetamide (LiCl/DMAc) solvent and a surface-selective dissolution technique. OPEFB is an abundant yet underutilized renewable resource in Malaysia. In response to the growing demand for sustainable, high-performance materials, this study investigates into the impact of process condition parameters on the tensile, structural, thermal, and water interaction characteristics of ACC films. The fabrication of ACC involved utilizing process condition parameters formulations with dissolution times of 5, 15, 30, and 45 minutes, combined with initial cellulose concentrations of 1%, 3%, and 5%. A straightforward pulping, bleaching, and solution casting technique were employed to extract OPEFB cellulose pulp, ensuring efficient film fabrication. Tensile analysis reveals that the best combination of 3% initial cellulose concentration and 15 minutes dissolution time results in ACC films with superlative tensile strength (44.41 MPa) and Young's modulus (3.26 GPa). X-ray diffraction (XRD) studies reveal a structural transition of the dissolved cellulose from cellulose I to cellulose II, while also confirming the coexistence of both cellulose I and II phases., leading to a notable decrease in the degree of crystallinity observed in ACC films. The Fourier transmission infrared spectroscopy (FTIR) analysis further supports the crystallinity assessment conducted with XRD, utilizing the total crystallinity index (TCI) results. Thermogravimetric study using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) shows a marginal decrease in thermal stability

with an increase in dissolution time. Examination of maximum temperature ( $T_{\max}$ ) in relation to dissolution time indicates a consistent decline in  $T_{\max}$  as dissolution time increases, attributed to enhanced breakdown of hydrogen bonds and diminished crystallinity. XRD and FTIR findings suggest a correlation between reduced crystallinity and decreased thermal stability. Scanning electron microscopy (SEM) investigations confirm the shift in the film composite's failure mode and an improved surface with fewer voids. Building on this, the research explores the impact of dissolution time and initial cellulose concentration on water absorption and biodegradation properties of ACC films. Water absorption reveals a complex interplay among dissolution time, initial cellulose concentration, and hydrophilicity, with ACC films showing unique water absorption behavior. Biodegradation studies underscore the significant roles of initial cellulose concentration and dissolution time, with both factors influencing degradation rates. Higher initial cellulose concentrations are associated with slower degradation rates. This comprehensive investigation into the multifaceted properties of OPEFB-based ACC films provides valuable insights into their tensile, structural, thermal, water absorption and soil biodegradability characteristics. The findings enhance sustainable material design understanding and offer versatile applications, underscoring the need to optimize processing parameters for eco-friendly composite development.

# CHAPTER 1

## INTRODUCTION

### 1.1 Background of the study

The global shift towards sustainable development has sparked a growing concern over the environmental impacts of conventional plastics and synthetic composites. Plastics, predominantly derived from fossil fuels, have contributed significantly to pollution, with millions of tonnes accumulating in landfills and oceans every year (Courtene-Jones et al., 2022;). The need for alternatives has never been more urgent, as the depletion of non-renewable resources and the ecological damage caused by plastic waste continue to rise (Foroughi et al., 2021). In response, researchers are turning to natural, renewable resources to develop biodegradable materials or biocomposites that can replace traditional plastics while minimizing environmental harm (Andrew & Dhakal. 2022; Ilyas et al., 2022).

Among these alternatives, all cellulose composites (ACC) have emerged as a promising solution. ACCs are fully bio-based materials, consisting solely of cellulose, the most abundant biopolymer on earth (Duchemin et al., 2009). With their impressive mechanical properties, biodegradability, and renewability, ACCs have the potential to reduce the dependence on synthetic composite in various industries. However, despite their potential, the commercial application of ACCs remains limited due to challenges in optimizing processing parameters. Factors such as cellulose concentration, dissolution time, and temperature play a critical role in determining the final properties of ACC films, necessitating further investigation into these variables to unlock the full potential of ACCs (Huber et al., 2011).

Malaysia's palm oil industry produces vast amounts of oil palm empty fruit bunch (OPEFB), a major agricultural byproduct that is rich in cellulose. While OPEFB

has primarily been used in low-value applications like paper production, its potential as a sustainable source for ACC production has garnered attention in recent years. With millions of tonnes of lignocellulosic waste generated annually, OPEFB presents a valuable opportunity to develop high-performance, eco-friendly composites (Umar et al., 2021; Suriani et al., 2021). This study seeks to explore the viability of using OPEFB-derived cellulose to produce ACC films, focusing on optimizing the processing conditions to achieve desirable mechanical and physical properties. By refining these conditions, this research aims to contribute to the advancement of sustainable materials and the efficient utilization of agricultural waste.

## **1.2 Problem statement**

Malaysia's annual production of over 23 million tonnes of oil palm empty fruit bunch (OPEFB) biomass (Anuar et al., 2019) presents a largely untapped renewable resource, especially for applications in all cellulose composite (ACC) films. Current ACC fabrication methods rely on intricate and costly approaches, including microcrystalline cellulose (MCC) and nano-scale formulations, which are resource-intensive and require substantial energy and chemical input (Baghaei & Skrifvars, 2020). However, straightforward or facile methods using dissolved pulp remain underexplored, even though these techniques could significantly simplify production and reduce environmental impact (Chen et al., 2020). Developing a sustainable, efficient fabrication process for ACC films from OPEFB thus requires an optimized approach that carefully balances cellulose concentration and dissolution time key parameters that influence composite properties to enhance both ACC performance and the effective use of Malaysia's OPEFB biomass (Gea et al., 2018a; Zailuddin et al., 2020a, 2020b)

### **1.3 Objectives of this research**

This study aims:

1. To formulate the process condition parameters (initial cellulose concentration and dissolution time) of ACC films isolated from OPEFB using surface selective dissolution and facile film preparation.
2. To characterize the effect of process condition parameters on the physico-chemical, tensile, thermal and water interaction properties of ACC films isolated from OPEFB.
3. To evaluate the best combination of process condition parameters on tensile strength of ACC films isolated from OPEFB.

### **1.4 Thesis Outline**

The first chapter introduces the study's focus on oil palm empty fruit bunch (OPEFB), an abundant yet underutilized waste from palm oil production, and its potential for developing sustainable all cellulose composites (ACC). The research aims to address challenges in processing OPEFB fibers, particularly optimizing cellulose dissolution time and concentration to improve the ACC's properties. The chapter outlines the problem, research objectives, and provides an overview of the thesis structure.

Chapter 2 provides an overview of research literature focusing on bio-derived materials, which includes a comprehensive discussion on ACC films. The chapter explores into the historical evolution of ACC films, tracing their development from synthetic to sustainable composites. It explores the crucial aspects of cellulose dissolution and regeneration, emphasizing essential contributions in the field. The synthesis methods for ACC films are detailed, with a specific focus on solvent-based

approaches and the diverse raw materials used. Additionally, the chapter examines processing parameters influencing ACC films fabrication and introduces various characterization techniques. The literature review concludes by addressing future trends and challenges in ACC films research, including potential applications and environmental considerations.

Chapter 3 comprehensively details the research methodology employed for the fabrication of ACC films and its characterization. This encompasses a thorough exploration of the material and solvent selection process, the chosen cellulose dissolution route, and the intricacies of experimental procedures. The chapter serves as a comprehensive guide, providing insights into the meticulous steps taken in the fabrication of ACC films, ensuring transparency, and facilitating a deep understanding of the research process.

In chapter 4, the findings of the research are presented, allowing for a detailed comparison with existing literature. The chosen processing condition parameters are discussed in-depth, providing interpretations and implications for the field. The chapter reveals the best combination of parameters to achieve the best tensile properties and offers insight into the physico-chemical, mechanical, thermal, and water interaction of the composite's properties.

The concluding chapter 5 integrates the key findings from the research, presenting a comprehensive summary. It emphasizes the contributions of the study to the field of ACC films and suggests recommendations for future research directions. The chapter concludes with a thoughtful reflection on the overall significance of the research and its potential impact on advancing sustainable composite materials.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 All cellulose composite historical outline

All cellulose composite (ACC) films, a distinctive category of biocomposites, are characterized by both the matrix and reinforcement phases derived exclusively from cellulose (Huber et al., 2011). This unique class of materials has a rich historical development intertwined with the broader evolution of biocomposites and sustainable materials. The mid-20th century marked the early exploration of ACC films, with researchers delving into the potential of cellulose as a reinforcing material (Acharya et al., 2021a; Debnath et al., 2021). Pioneering work by Nishino et al. (2004) laid the foundation for ACC films by introducing the concept of using chemically identical cellulosic materials for both matrix and reinforcement, emphasizing the significance of achieving ideal chemical bonding.

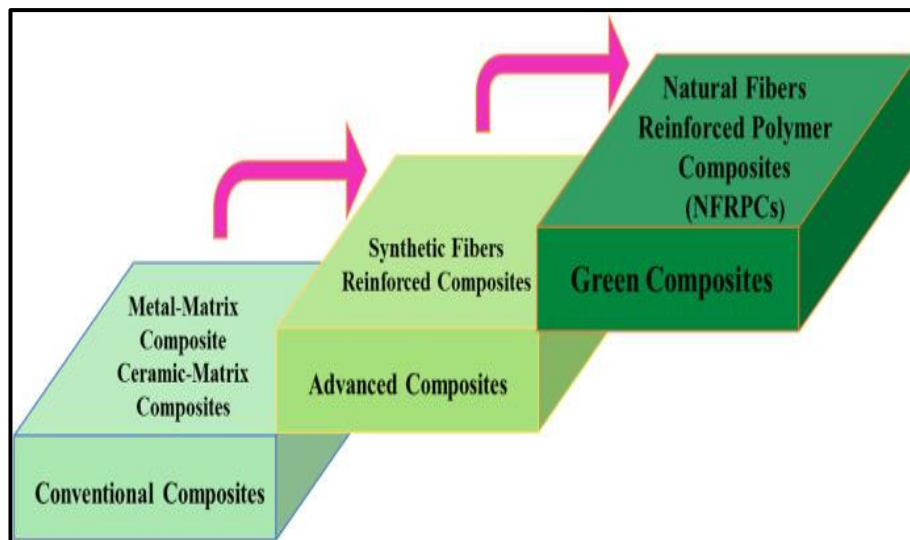


Figure 2.1 Evolution of composite materials: from synthetic to sustainable alternatives

Figure 2.1 depicts the progression of composite materials, transitioning from synthetic options to sustainable alternatives. Initially, composite materials were largely

dominated by synthetic polymers derived from petroleum sources. These synthetic composites offered exceptional mechanical properties but have led to environmental concerns due to their non-biodegradable nature. Consequently, there has been a growing interest in biocomposite materials, which utilize renewable resources and biodegradable matrices (Andrew & Dhakal, 2022). This transition marks a shift towards more sustainable alternatives in response to the escalating concerns over plastic pollution and environmental degradation.

Biocomposites, featuring natural fibers such as cellulose within biodegradable polymer matrices, represent a crucial advancement in sustainable material engineering (Zwawi, 2021). Cellulose, abundant in plant cell walls, offers inherent advantages such as renewability and biodegradability, making it an ideal candidate for composite materials (Debnath et al., 2021; Joseph et al., 2020; Tanpichai et al., 2020, Boonmahitthisud et al., 2022). The integration of cellulose fibers into polymer matrices has resulted in the development of biocomposites, which exhibit promising mechanical properties while addressing environmental concerns associated with synthetic counterparts.

Recently, there has been a resurgence of interest in natural fiber-reinforced polymer composites, driven by environmental concerns and supported by government initiatives. Natural fibers such as wood, jute, hemp, and flax offer advantages over synthetic fibers, including biodegradability, higher specific strength and stiffness, and reduced energy consumption during processing. However, challenges such as poor interfacial adhesion and susceptibility to moisture limit their widespread use (Nazrin et al., 2020; Jumaidin et al., 2020; Sari et al., 2020). To overcome these drawbacks, researchers have proposed innovative solutions and explored various strategies to enhance the compatibility of cellulose with hydrophobic matrices commonly used in

composite materials. These strategies include physical and chemical treatments of both fiber and matrix components, as well as the utilization of cellulose in micron and nanoscale formats (Amiandamhen et al., 2020). While these methods have shown promise in improving the properties of bio-based composites, they often come with increased costs and complexities in the manufacturing process (Duchemin et al., 2009).

To overcome these challenges as stated earlier, the new concept of green composite called all cellulose composites (ACC) draws inspiration from traditional single polymer composites (SPC) (Capiati et al., 1975; Nishino et al., 2004; Baghaei & Skrifvars, 2020). Unlike traditional synthetic and many bio-based composites, which rely on synthetic polymers derived from fossil fuels either for reinforcement or as a matrix, ACCs are composed entirely of cellulose, the most abundant biopolymer on Earth ( Gindl & Keckes, 2005; Duchemin et al., 2009). Cellulose boasts a myriad of desirable properties, including mechanical strength, chemical stability, biodegradability, and renewability, making it an ideal candidate for sustainable materials (Zailuddin et al., 2020a; Joseph et al., 2020; Acharya et al., 2021; Debnath et al., 2021; Boonmahitthisud et al., 2022).

The progression of composites has unfolded from synthetic compositions, transitioning through biocomposites, culminating in green composites, and ultimately leading to the emergence of a new generation of single-polymer composites. This novel composite has undergone further evolution, ultimately giving rise to the innovative all cellulose composite, as outlined in Table 2.1.

Table 2.1 Historical development timeline of ACC films.

<b>Year</b>	<b>Research</b>	<b>Remark</b>	<b>Reference</b>
1975	Introduced and developed single polymer composite (HDPE)	Thermoplastic	Capiati et al., 1975
1996	Developed single polymer composite, All-polypropylene composite (PP)	Thermoplastic	El Maaty et al., 1996
2004	Introduced and developed single polymer composite, all cellulose composite (ACC), two-step method	Cellulose	Nishino et al., 2004
2005	Developed single polymer composite, all cellulose composite (ACC), one-step method	Cellulose	Gindl & Keckes, 2005

Capiati and co-workers introduced and developed the concept of single polymer composites utilizing high-density polyethylene (HDPE) as the primary thermoplastic matrix material (Capiati & Porter, 1975). Building upon this foundation, El Maaty et al. (1996) further expanded the repertoire of single polymer composites by developing an all-polypropylene composite (APP). By utilizing polypropylene as both the matrix material and reinforcement, this advancement showcased the potential for enhancing compatibility and mechanical performance within a homogeneous composite structure. The introduction of APP composites represented a significant milestone in composite material engineering, offering improved processability and recyclability compared to traditional composite systems.

The late 20th and early 21st centuries witnessed a surge in interest in sustainable materials, driven by environmental concerns and the quest for eco-friendly alternatives (Joseph et al., 2020; Tanpichai et al., 2020, Debnath et al., 2021; Boonmahitthisud et al., 2022). This period marked a paradigm shift towards greener

alternatives, with ACC films emerging as a frontrunner in sustainable composite materials. Inspired by the success of single polymer composites like all-polypropylene composites, researchers began exploring the development of ACC films as a novel subcategory of biocomposites (Nishino et al., 2004; Gindl & Keckes, 2005).

In the realm of biocomposite materials, Nishino et al. (2004) pioneered the development of single polymer composites utilizing cellulose as the primary reinforcement material. Their work introduced and developed the concept of ACC films utilizing a two-step method, wherein cellulose fibers were chemically treated and dispersed within a cellulose matrix. Subsequently, Gindl et al. (2005) further refined the fabrication process by introducing a one-step method for producing ACC, demonstrating improved efficiency and scalability in composite manufacturing.

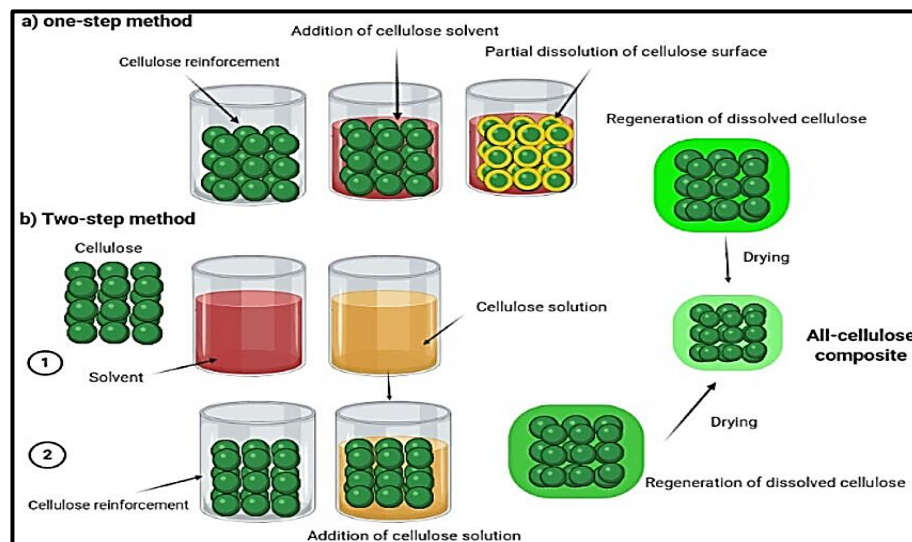


Figure 2.2 Schematic representation of ACC films preparation (a) one-step method, and (b) two-step method

This innovative strategy, showcased through two methods in Figure 2.2, leveraged the intrinsic mechanical properties and biodegradability of cellulose, providing a sustainable substitute for synthetic composites. The first monocomponent

composite based on cellulosic material, the ACC films, was developed as an innovative approach to address interfacial adhesion challenges inherent in traditional biocomposites. As research progressed, a focus on refining processing techniques became evident. Dissolution processes, particularly those utilizing LiCl/DMAc solutions, were optimized to enhance the interfaceless concept. The interfaceless nature of ACC films, where boundaries between reinforcement and matrix are indistinct due to ideal chemical bonding, became a focal point for researchers striving to improve overall performance (Huber et al., 2011).

The historical trajectory of ACC films has not been without challenges. Issues related to in situ factors, varying cellulose sources, solvents, and processing routes have posed significant hurdles (Huber et al., 2012). Nevertheless, these challenges have spurred innovations in cellulose isolation techniques, dissolution parameters, and fabrication processes. The current state of ACC films research reflects a dynamic field with ongoing efforts to overcome challenges and further optimize properties. In summary, the development of ACC films reflects a journey marked by milestones, challenges, and continuous innovation. From the early foundations to the current state of research, ACC films have emerged as promising candidates for sustainable, green composite materials. As the field advances, a nuanced understanding of historical developments provides a valuable foundation for shaping the future of ACC films.

### **2.1.1 From synthetic to sustainable composite**

The primary reasons for the transition from synthetic to bio- and green composites are largely attributed to environmental impact of plastic pollution and the depletion of fossil fuels (Abushammala & Mao, 2020; Sabaruddin et al., 2020; Baghaei & Skrifvars, 2020). However, the exploration of all cellulose composite as a new generation of green composite presents numerous reasons for investigation. One

crucial aspect of the development of ACC films is its biodegradability, compostability and recyclability properties. The transition from non-biodegradable composites to biodegradable ones is pivotal for fostering a healthier environment by mitigating plastic pollution.

Biodegradability stands as a critical parameter in evaluating the environmental impact of composite materials, particularly in the context of mitigating plastic pollution and promoting sustainability (Sinha, 2024). Synthetic composites, predominantly derived from petroleum-based polymers, exhibit limited biodegradability due to their synthetic nature and resistance to enzymatic degradation by microorganisms. These materials often persist in the environment for hundreds to thousands of years, contributing significantly to global plastic pollution (Sabaruddin et al., 2020). In contrast, biocomposite materials, which integrate natural fibers such as cellulose within biodegradable polymer matrices, offer enhanced biodegradability compared to synthetic counterparts. The inherent biodegradability of natural fibers, combined with the biodegradable matrix materials, enables biocomposites to undergo enzymatic degradation by microorganisms, ultimately breaking down into simpler organic compounds over time.

Furthermore, green composites represent a subset of biocomposite materials that prioritize sustainability by incorporating renewable resources and environmentally friendly manufacturing processes. Green composites typically exhibit superior biodegradability compared to traditional synthetic composites. Moreover, green composites have achieved remarkable milestones, boasting 100% biodegradability, recyclability, and compostability (Vázquez-Núñez et al., 2021). These materials undergo rapid degradation into non-toxic substances, minimizing their

environmental footprint and facilitating their integration into circular economy models.

In addition to their environmental benefits, biocomposite materials offer cost-effectiveness due to the abundant availability of cellulose, a primary component in their composition. Cellulose is sourced from renewable plant-based materials, making it a cost-efficient alternative to petroleum-based polymers used in synthetic composites. The creation of ACC films further underscores the sustainability and cost-effectiveness of biocomposites. ACC films is produced by integrating cellulose fibers as both the reinforcement and matrix material, offering a versatile and economically viable solution for various applications.

In summary, the comparison of biodegradability among synthetic composite, biocomposite, and green composite highlights the critical role of material composition and manufacturing processes in shaping environmental sustainability. While synthetic composites pose significant challenges due to their limited biodegradability and persistence in the environment, biocomposite and green composite materials offer promising solutions by leveraging renewable resources and biodegradable constituents. As ACC films continue to gain attention, their unique properties position them as integral components in the pursuit of green composite materials. From early foundations to ongoing research endeavors, the progress of ACC films signifies a broader shift toward sustainability in composite material design.

### **2.1.2 Chemical structure and sources of cellulose**

The successful synthesis of ACC films relies significantly on the careful choice of raw materials and cellulose sources, as these factors play an essential role in shaping the properties and sustainability of the eventual composites. Extensive research has been conducted on utilizing cellulose as the sole component in ACC films,

encompassing various sources such as plant cellulose, wood, non-wood cellulose, and bacterial cellulose. Therefore, gaining a comprehensive understanding of the cellulose structure is imperative for grasping the intricacies of ACC films themselves.

The initial identification and isolation of cellulose from green plants were credited to Anselme Payen (1795-1871) (Klemm et al., 2005). Cellulose, an omnipresent natural polymer, is essential for maintaining the structural strength of plant cell walls and represents a plentiful and renewable raw material. Cellulose is present not only in plants like wood and cotton but also in a diverse range of organisms including algae, fungi, bacteria, and tunicates. Structurally, as depicted in Figure 2.3, cellulose is a rigid linear polysaccharide, consists of repeating units of  $\beta$ -D-glucopyranose interconnected by 1-4-glycosidic bonds. Cellubiose refers to a molecular structure where two anhydroglucose units are connected through a  $\beta$ -1,4-glycosidic linkage (Pullawan, 2012).

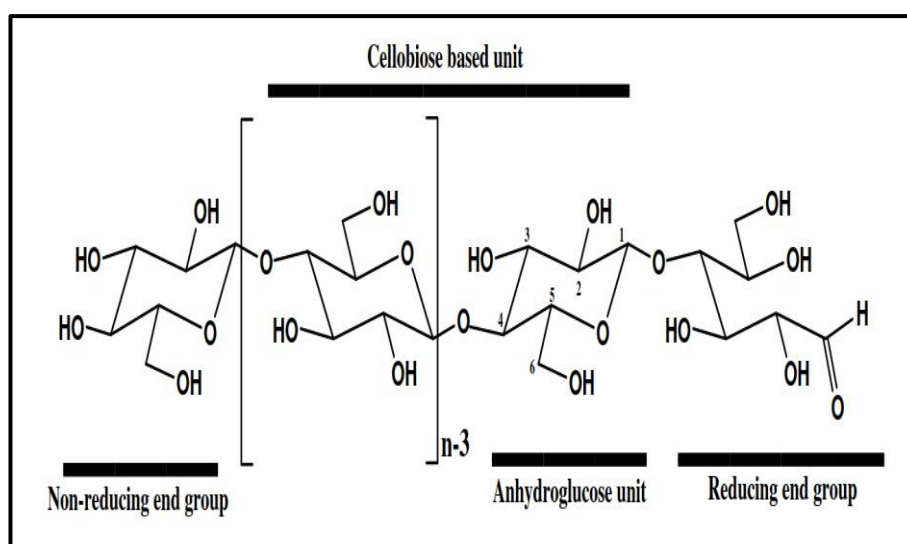


Figure 2.3 Molecular structure of cellulose (Klemm et al., 2003)

A solitary glucose unit (hexose) can adopt either an  $\alpha$  or  $\beta$  configuration, determined by the arrangement of hydroxyl (OH) groups. The presence of hydroxyl

groups on each glucose ring facilitates the formation of intramolecular and intermolecular hydrogen bonds, influencing cellulose's behavior of hydrophilicity. The consideration of cellulose allomorphs adds an additional layer of complexity, contributing to the diverse range of physical and chemical properties observed in cellulose (Moran et al., 2007).

Cellulose exists in different allomorphic forms, commonly referred to as cellulose allomorphs. Four different forms of cellulose allomorphs are identified and referred to as cellulose I, II, III, and IV. Understanding their differences is key for optimizing cellulose-based materials in industrial applications. Figure 2.4 illustrates the different crystalline structures of cellulose, focusing on Cellulose I and Cellulose II. Cellulose I, also known as native cellulose, is the most crystalline form of cellulose and exists in two structural variations:  $I\alpha$  with a triclinic unit cell and  $I\beta$  with a monoclinic unit cell (Atalla & Vanderhart, 1984).

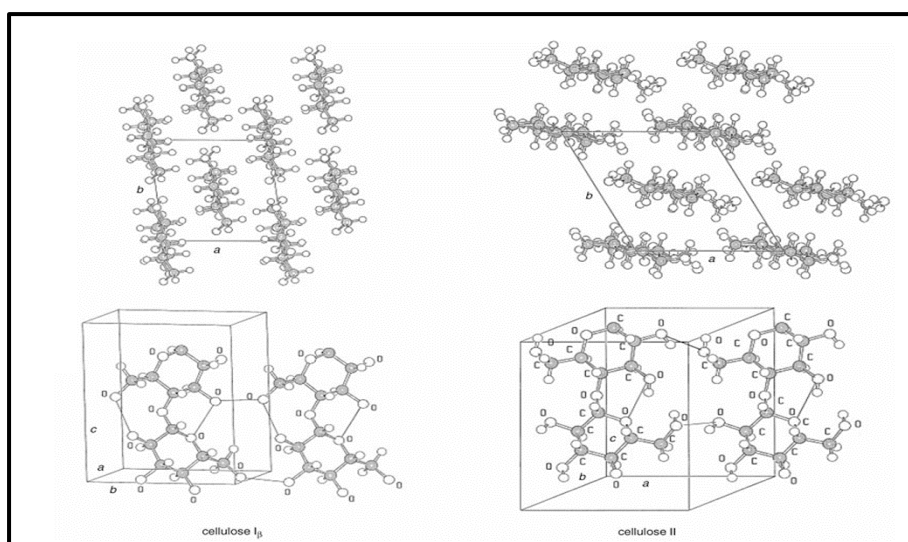


Figure 2.4 Hydrogen bonding structures of both cellulose I and II (Klemm et al., 2005)

The ratio of  $I\alpha$  to  $I\beta$  regions can vary depending on the cellulose source, with lower plants like *Valonia* predominantly exhibiting  $I\alpha$ , while higher plants such as

cotton cellulose mainly display I $\beta$  (Heiner et al., 1995). Cellulose I $\beta$  is more stable than I $\alpha$  due to differences in hydrogen bonding arrangements (Sugiyama et al., 1990). In I $\beta$ , both intermolecular and intramolecular bond angles are closer to 180° compared to I $\alpha$  (Nishiyama et al 2002, 2003). These differences in crystallographic structure and hydrogen bonding patterns between cellulose I $\alpha$  and I $\beta$  contribute to variations in cellulose fiber properties. Notably, intrachain O2H-O6 bond distances are shorter in I $\alpha$ , while interchain O6H-O3 bond distances are shorter in I $\beta$  (Šturcová et al., 2004). Additionally, the arrangement of cellulose chains along crystallographic planes (110), (100), and (010) for I $\alpha$ , and (200), (110), and (1-10) for I $\beta$  affects the overall structural stability and mechanical performance of cellulose fibers.

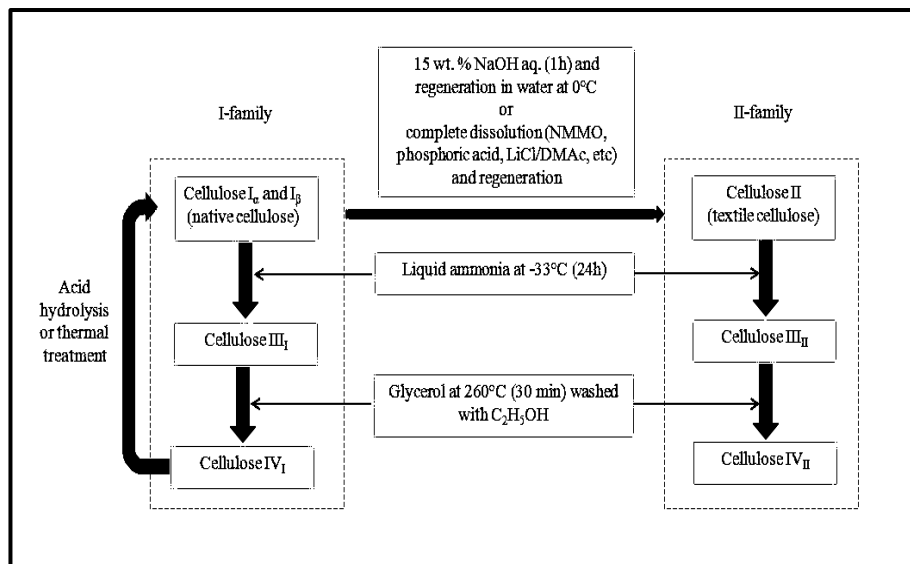


Figure 2.5 The conversion mechanism of cellulose (Huber et al., 2012)

Cellulose II, the most thermodynamically stable form, is synthesized via the mercerization or regeneration of cellulose I and serves as the predominant constituent in man-made cellulose fibers such as rayon and Lyocell (Ranby 1951). Its structure is characterized by an antiparallel arrangement of cellulose chains, resulting in the presence of reducing ends at both crystal ends (French & Johnson, 2007). Cellulose

III, generated from cellulose I or II through liquid ammonia treatment, can yield either the III<sub>I</sub> or III<sub>II</sub> structure, while cellulose IV<sub>I</sub> and IV<sub>II</sub> are derived from cellulose III by glycerol-induced heating (Huber et al., 2012). These transformations, illustrated in Figure 2.5, underscore the versatility and significance of cellulose as a renewable biomaterial with diverse applications.

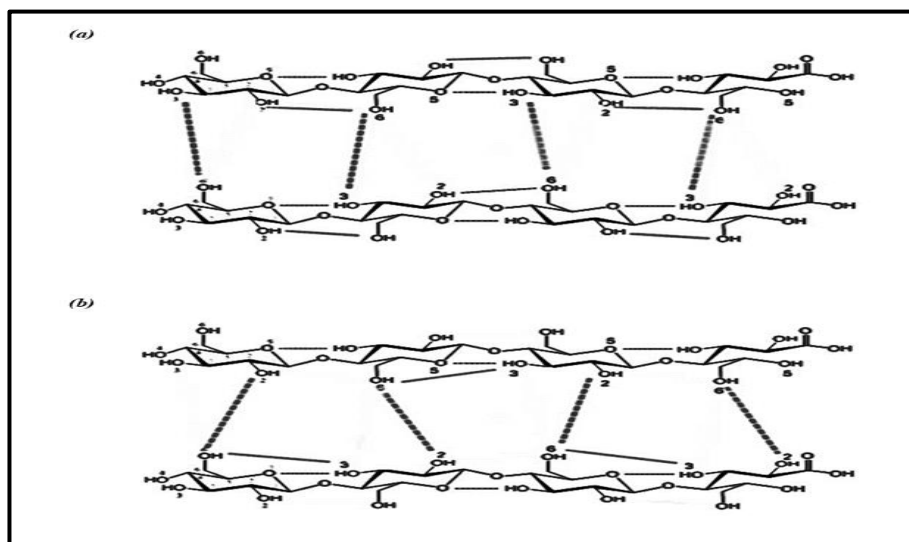


Figure 2.6 The chain configurations of (a) cellulose I and (b) cellulose II, with intermolecular and intramolecular hydrogen bonding represented by dotted and solid lines, respectively (Pullawan 2012)

Variations in the mechanical characteristics of cellulose allomorphs stem from disparities in their molecular structures (Huber et al. 2012). Cellulose I exhibit a semicrystalline nature, where amorphous regions form a thin layer between single microfibrils, aligned longitudinally within the fiber, known as the micellar or fringe fibrillar model. The stability of amorphous cellulose in moist environments is compromised, often leading to its recrystallization into cellulose II (Ciolacu et al., 2011a, 201b). The fundamental structural unit of cellulose comprises parallelly arranged crystalline chains, held together by intermolecular and intramolecular hydrogen bonding of hydroxyl (OH) groups along the cellulose chain, reinforcing the

rigidity and strength of cellulose molecules (Richardson & Gorton 2003). These chains assemble into extended molecular segments, termed elementary fibrils. Figure 2.6 illustrates the chain conformations of cellulose I and II.

Hydrogen bonding in cellulose I and II occurs at distinct positions. In cellulose I, intramolecular hydrogen bonding occurs at O(3)H-O(5) and O(2)H-O(6), while intermolecular hydrogen bonding takes place at O(3)H-O(6). Conversely, cellulose II forms intramolecular hydrogen bonds at O(3)H-O(6) and O(3)H-O(5), with intermolecular hydrogen bonding occurring at O(2)H-O(6). Both cellulose I and II exhibit intramolecular hydrogen bonds at O(3)H-O(5), contributing to their linear and rigid chain structures. The primary difference lies in interchain bonding, where cellulose I predominantly features hydrogen bonding at O(3)H-O(6), while cellulose II exhibits dominant bonding at O(2)H-O(6).

Having examined cellulose's molecular complexities, the focus now turns to its diverse sources especially cellulose source using in this study and thesis. Understanding where cellulose comes from is crucial for its industrial use and environmental sustainability. Historically, studies on developing ACCs have explored sources from non-wood based cellulose or biomass such as flax (Chen et al., 2020), cotton (Cheng et al., 2018), canola straw (Yousefi. et al., 2011), bagasse (Ghaderi et al., 2014), hemp (Chen K et al., 2020), pineapple leaf (Tanpichai et al., 2016), and Napier grass (Kumar et al., 2018) as alternative cellulose sources for ACC films, contributing to sustainable biomass utilization. The transition from utilizing wood-based cellulose to biomass waste serves a dual purpose: mitigating forest destruction and promoting sustainable resource utilization. Biomass waste, such as agricultural residues, food waste, or by-products from various industries, presents an attractive

solution. By redirecting focus towards biomass waste, it can minimize reliance on wood-derived cellulose, thereby reducing pressure on forests and ecosystems.

In the context of large-scale agricultural waste, the significant role of palm oil waste, particularly from the Malaysian palm oil industry, comes into play. Malaysia, one of the world's leading producers of palm oil production, generates 5.4 million-hectare oil-palm plantation, which contributes to about 90% of the country's lignocellulosic biomass waste (Loh, 2017), underscoring the potential of this waste material as a valuable resource for cellulose production (Norrrahim et al., 2019).

The Malaysian Palm Oil Board (MPOB) indicated a growth in Malaysian plantations, i.e., from 400 hectares in 1920 to over five million today (Loh, 2017; Suriani et al., 2021). The oil palm (OP) business produces an estimated 15 million tonnes of lignocellulose wastes annually, such as trunks (OPT), fronds (OPF), and empty fruit bunches (OPEFB), which make up a major economic pillar for the country (Khalil et al., 2011). These plantations generate around 90% of Malaysia's lignocellulosic biomass waste.

Generally, when processing one tonne of fresh fruit bunch (FFB), palm oil companies produce various types of waste, including empty fruit bunch (EFB) (23%), mesocarp fiber (MF) (12%), palm kernel shell (PKS) (5%), and palm oil mill effluent (POME) (60%) (Umar et al., 2021). Despite its abundance and potential as a candidate source for ACC films, the application of oil palm lignocellulosic waste in industrial composites has been hindered by challenges related to the lack of research, particularly regarding processing condition parameters. Currently, it is utilized to some extent in pulp and paper production and in the manufacturing of wood composite products (Singh et al., 2013), both of which represent low-value applications.

Figure 2.7 illustrates the different types of fibers that can be obtained from various parts of the oil palm tree. The focus is on the oil palm empty fruit bunch (OPEFB) fiber, which is in the middle right. OPEFB fibers come from the bunches left over after the oil-rich fruitlets are removed. These fibers are high in cellulose and are often used in making biodegradable materials, reinforcing composites, or as a source for biofuels. The other parts of the tree such as the fronds, mesocarp, and trunk also provide useful fibers, but OPEFB is particularly valuable for sustainable applications due to its abundance and high fiber content.

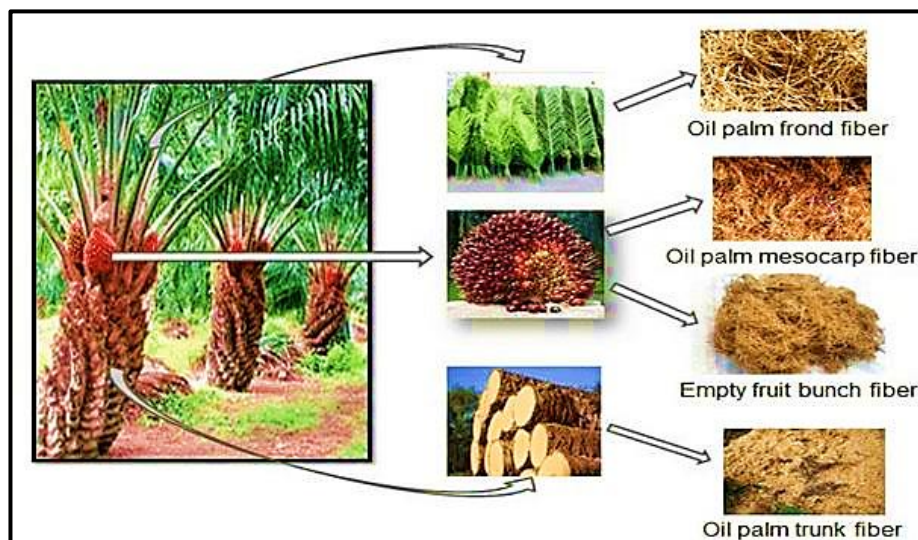


Figure 2.7 Oil palm empty fruit bunch

These fibrous materials are primarily composed of cellulose, hemicellulose, lignin, and minor components. Cellulose, the main structural element, provides strength and rigidity to OPEFBs, while hemicellulose acts as a binding agent, binding cellulose fibers together. Lignin, a complex polymer, fills the gaps between cellulose and hemicellulose, offering structural support and resistance to degradation. Additionally, OPEFBs may contain extractive compounds such as fats, waxes, and phenolics in small amounts, which contribute to their overall chemical composition.

Table 2.2 presents a comprehensive overview of the chemical composition of OPEFBs based on various research findings. Overall, the chemical composition of OPEFBs makes them a valuable renewable resource for industries including bioenergy, pulp and paper, and composite materials production. With their abundant cellulose content and availability as a byproduct of palm oil extraction, OPEFB hold promise as a sustainable feedstock for various applications.

Table 2.2 A comprehensive overview of the chemical composition of oil palm empty fruit bunches, drawing from various findings in prior research

Chemical composition			References
Cellulose (%)	Hemicellulose (%)	Lignin (%)	
51.10	18.90	21.10	Hassan et al., 2020
49.63	21.32	19.12	Aguilar et al., 2022
37.50	11.60	18.50	Fapohunda et al., 2023

In summary, the provided data highlights that the Malaysian palm oil industry produces a substantial volume of biomass, positioning it as a valuable source of cellulose in development of ACC films product. Furthermore, only a few studies had examined the generation of ACC from oil palm wastes such as OPEFB in the past 10 years (Gea et al., 2018a, 2018b; Zailuddin et al., 2020a, 2020b). The exploration of OPEFB as a cellulose source highlights the potential for transforming agricultural by-products into value-added materials, promoting a more circular and sustainable approach within the palm oil industry.

## **2.2 Synthesis Methods for ACC**

The synthesis of ACC films represents an innovative approach in composite material science, where cellulose serves both as the matrix and reinforcement. An essential phase in ACC films fabrication involves the dissolution and subsequent regeneration of cellulose. This methodology can be comprehended through an exploration of cellulose itself, which is the sole component in ACC films, as previously mentioned in section 2.1.2. Cellulose, a linear polysaccharide consisting of repeating glucose units, is highly insoluble in most conventional solvents due to its strong intra- and intermolecular hydrogen bonding network, thereby rendering it resistant to melting. Consequently, cellulose can only be tailored through dissolution, as opposed to conventional melting processes.

Specialized techniques are employed to fabricate ACCs, involving modifications of cellulose's dissolvability characteristics to achieve the desired composite structure. This includes complete dissolution followed by mixing with additional reinforcing cellulosic material, and selective cellulose dissolution to create an in-situ matrix phase around the residual fiber core (Nishino et al., 2004, Nishino & Arimoto, 2007; Gindl & Keckes, 2006).

### **2.2.1 Cellulose dissolution and regeneration**

Figure 2.8 illustrated schematic of cellulose dissolution and regeneration. The engineering and objective behind this approach involve the transformation of cellulose into a liquid state through dissolution, followed by the reformation of the dissolved cellulose into a specific solid form. Cellulose dissolution entails breaking down cellulose, a polysaccharide found in plant cell walls, into its individual molecular components and dispersing them in a solvent to create a solution. This process involves disrupting the robust intra- and intermolecular hydrogen bonds within cellulose,

leading to its transformation into a liquid state (Medronho & Lindman, 2015). The mechanism of cellulose dissolution depends on the solvent used and the specific conditions of the dissolution process.

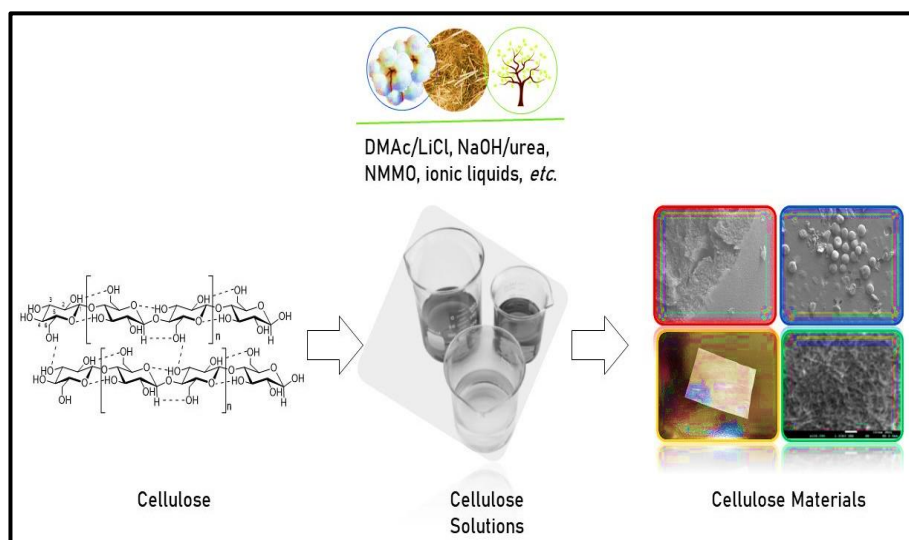


Figure 2.8 Schematic of cellulose dissolution and regeneration (Acharya et al., 2021a)

To date, researchers have explored two primary methods for dissolving cellulose: the viscose method and the non-viscose method. In the viscose method, cellulose is transformed into sodium cellulose xanthate using carbon disulfide ( $\text{CS}_2$ ), a chemical compound used in the viscose process for producing rayon and cellophane. This cellulose xanthate is soluble in  $\text{NaOH}$ , allowing to produce fibers or films using wet spinning techniques. Conversely, in the non-viscose process, cellulose is dissolved using various solvents such as urea/ $\text{NaOH}$ , N-methyl morpholine-N-oxide (NMMO),  $\text{LiCl}/\text{N}$ , N-dimethylacetamide (DMAc), and ionic liquids (ILs). All these methods break the intermolecular hydrogen bonds that hold them together in the solid state (Huber et al., 2012; Chen et al., 2020; Acharya et al., 2021a, 2021b).

Following the dissolution of cellulose, the subsequent phase of regeneration is the synthesis of ACC films. Through this process, the dissolved cellulose is recovered and reconstituted into a solid state, typically achieved through precipitation or coagulation methods (Duchemin et al., 2009; Huber et al., 2012). During regeneration, the solvent is carefully extracted from the cellulose solution, facilitating the reformation of cellulose chains and the formation of the desired solid structure. This meticulous procedure allows for the manipulation of cellulose at the molecular level, enabling the fabrication of tailored materials with specific properties and applications. The choice of regeneration method significantly influences the properties of the regenerated cellulose, impacting factors such as crystallinity, morphology, and mechanical strength, thus shaping the final characteristics of the resultant material.

Additionally, the dissolved cellulose solution can be further customized by incorporating cellulose nanoparticles or other additives to enhance specific properties of the composite material (Mohan et al., 2020). The regenerated cellulose matrix is then reinforced with cellulose fibers using various processing techniques such as casting, spinning, or compression molding (Tanpichai et al., 2016). This reinforcement process results in the formation of ACC films with superior mechanical properties, biodegradability, and environmental sustainability compared to traditional synthetic composites. The integration of cellulose at both the molecular and macroscopic levels offer a promising avenue for the development of sustainable materials with diverse applications across industries.

As delineated in section 2.1, the preparation of ACC films involves two primary techniques: the two-step method and the one-step method. These methods are alternatively referred to by various names in previous research. The two-step method is commonly known as fully dissolved, whereas the one-step method is sometimes

denoted as surface selective dissolution or partially dissolved (Li et al., 2018). Despite their nomenclatural diversity, all these techniques entail a series of steps involving cellulose dissolution and subsequent regeneration processes. Additionally, the choice of solvents plays a crucial role in cellulose dissolution, with LiCl/DMAc solutions proving instrumental in achieving efficient cellulose dissolution for ACC films (Soykeabkaew et al., 2008; Qin et al., 2008). The impact of different solvent systems on the dissolution process will be further discussed in the next section.

In the fully dissolved approach, cellulose is completely dissolved in a suitable solvent, resulting in a homogeneous solution. Techniques for fully dissolved ACC include solution casting, electrospinning, and 3D printing. Solution casting involves casting the cellulose solution into a mold followed by solvent evaporation to obtain a solid film. Electrospinning utilizes an electric field to draw a continuous jet of the cellulose solution into nanofibers, collected on a substrate (Anusiya & Jaiganesh, 2022). 3D printing involves layer-by-layer deposition of the cellulose solution to create intricate structures (Firmanda et al., 2022). Fully dissolved ACC films exhibit excellent mechanical properties and uniformity, making them suitable for applications in biomedical scaffolds, packaging materials, and electronics.

Alternatively, in the partially dissolved approach, cellulose is partially dissolved, resulting in a heterogeneous mixture of dissolved and undissolved cellulose. Preparation techniques for partially dissolved ACC films include compression molding, and solvent evaporation. Compression molding compresses a mixture of partially dissolved cellulose and additives into a mold under heat and pressure. Solvent evaporation involves casting a mixture of partially dissolved cellulose and additives followed by solvent removal to obtain the composite material. Partially dissolved ACC