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Recent Advances in TEMPO-oxidized Cellulose Nanofibers and Regenerated Cellulose Films from Food by-product Biomass: Mechanisms, Properties, and Applications

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Abstract The environmental impact of petroleum-based plastics packaging continues to grow, increasing attention has been directed toward the development of sustainable materials derived from renewable biomass. Cellulose-based biomass from agricultural residues and food processing by-products has emerged as a promising alternative due to its abundance, renewability, and biodegradability. To enhance the processability and applicability of cellulose derived from such sources, recent studies have focused on chemical modification techniques such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO)-mediated oxidation, as well as the use of advanced solvent systems including ionic liquids for the production of regenerated cellulose (RC) films. This review explores the fundamental principles and mechanisms of TEMPO-mediated oxidation and highlights the characteristics and potential applications of TEMPO-oxidized cellulose nanofibers (TOCNFs) derived from various biomass sources. In addition, it discusses the fabrication and performance of TOCNF composite films, major cellulose solvent systems and their dissolution mechanisms, and the properties and applicability of RC films.

Keywords Cellulose-based biomass, Food by-products, TEMPO-mediated oxidation, Regenerated cellulose film, DMAc/LiCl solvent system, Sustainable packaging

1. Introduction

Cellulose-based biomass, including cellulose or lignocellulose derived from agricultural, marine, and food processing wastes, is considered one of the most promising alternatives to non-renewable resources due to the environmental benefits such as biodegradability and sustainability[1-5]. However, cellulose-based biomass exhibits robust inter- and intra-molecular H-bonding due to chain stereoregularity and high density of the hydroxyl groups (-OH). As a result, they are insoluble in common organic solvents, which limits their applicability in various fields[6-8]. To overcome this limitation and improve the processability and applicability, appropriate mechanical and chemical modifications are necessary for converting cellulose-based biomass into nanomaterials[6-8]. Cellulose-based nanomaterials have aroused significant attention in the fabrication of packaging materials and other applications, due to their large surface area, high aspect ratio, excellent mechanical properties, biodegradability, and low coefficient of thermal expansion[9-11]. Mechanical treatments such as homogenization, grinding, blending, and ultrasonication have been successfully applied to produce these nanomaterials. However, such methods often require massive energy inputs, multiple processing steps, and involve high production costs[11-13]. To address these issues, pretreatment with chemicals such as acid hydrolysis, alkaline-acid treatment, and oxidation has been employed to reduce energy consumption[11,12]. Among them, acid hydrolysis with strong acids (e.g., HCl) is the most widely used technique. However, it presents several drawbacks, including equipment corrosion, wastewater treatment challenges, and environmental concerns[13].

To address these limitations, 2,2,6,6-tetramethylpiperidinyloxy (TEMPO)-mediated oxidation has attracted recent significant interest as an alternative chemical modification method for cellulose-based biomass[1,7,10-12]. Owing to the abundance of active -OH groups on its chains, cellulose is highly suitable for chemical modification. TEMPO-mediated oxidation selectively converts the primary -OH groups to carboxylate groups ($-COO^-$), thereby allowing for the controlled

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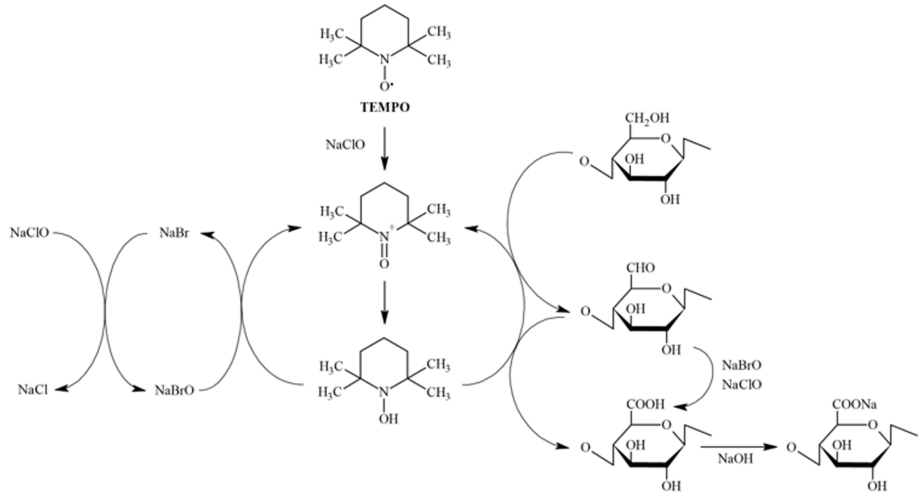

Fig. 1. Mechanism of TEMPO-mediated oxidation of cellulose[12,16-18].

spread of surface charge density and selective disintegration of cellulose fibers from plant cell walls. It not only reduces the energy required during mechanical treatment markedly but also enables the efficient production of cellulose-based nanomaterials. Furthermore, it can enhance the hydrophilicity of cellulose, allowing easy dissolution in solvent systems such as aqueous or ionic liquids[1,7,10-12].

Despite the increasing hydrophilicity through TEMPO-mediated oxidation, cellulose-based biomass cannot readily dissolve in water or polar organic solvents due to strong H-bonding and crystalline structure. Therefore, several specialized solvent systems, including *N*, *N*-dimethylacetamide (DMAc)/lithium chloride (LiCl), dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride, *N*-methylmorpholine-*N*-oxide (NMMO), and sodium hydroxide (NaOH)/urea have been employed to overcome this limitation[6-8,14]. These have enabled the processing of cellulose into regenerated cellulose (RC) films, which are obtained through a two-step process comprising its dissolution and subsequent regeneration by physical and chemical interactions[3,5,6,14,15].

Accordingly, this paper provides an overview of the recent advances achieved in the processing of cellulose-based biomass aimed at enhancing their processability and applicability. Particular emphasis is placed on TEMPO-mediated oxidation and the use of ionic solvents for the fabrication of RC films. First, we outline the principles and mechanisms underlying TEMPO-mediated oxidation. Second, we summarize recent studies addressing the application of TEMPO-oxidized cellulose in the packaging material industry. Third, we outline key solvent systems for cellulose and their respective dissolution mechanisms. Finally, we review the preparation methods and physicochemical properties of RC-based films, highlighting their potential in the field of fabricating sustainable packaging materials.

2. TEMPO-mediated oxidation

2.1. TEMPO-mediated oxidation mechanism

TEMPO is a commercially available, stable, water-soluble nitroxyl radical[11,16]. Moreover, compared to methods involving chemical modification of the -OH groups within cellulose chains, such as periodate oxidation or carboxymethylation using strong acids or harmful chemicals, TEMPO is a relatively safer with lower environmental impacts and toxicity[13,17]. Under mild reaction conditions, TEMPO-mediated oxidation can efficiently and selectively oxidize the C6-primary -OH groups of the cellulose chain to C6 sodium carboxylate groups (-COONa) without the need for high temperature and pressure[1,7,16-18].

The efficiency and selectivity of TEMPO-mediated oxidation strongly depend on the reaction conditions and the system employed. The TEMPO/sodium bromide (NaBr)/sodium hypochlorite (NaClO) oxidation system in water at pH 10-11 and room temperature is most commonly used[16,18]. In this system, TEMPO and NaBr are co-catalysts, while NaClO is the primary oxidizing agent, which is consumed during the reaction[16,18]. NaClO oxidizes the TEMPO to its active radical $TEMPO^+$ and NaBr to NaBrO. NaBrO further reacts with TEMPO to produce ($^+N=O$), which serves as an additional oxidizing agent. The nitronium ion facilitates the stepwise oxidation of C6 hydroxymethyl groups ($-CH_2OH$): first to aldehyde groups (-CHO), subsequently to a -COONa groups, as illustrated in Fig. 1[12,16-18].

2.2. Effect of TEMPO-mediated oxidation on the physicochemical and morphological properties of the cellulose extracted from diverse sources

TEMPO-mediated oxidation alters the chemical and morphological structure of cellulose, significantly influencing its

physicochemical properties. To assess the feasibility of Spent coffee grounds (SCGs) as an alternative to natural resources like wood, Kanai et al.[1] employed a TEMPO/NaBr/NaClO system to prepare TEMPO-oxidized cellulose nanofibers (TOCNFs) from SCGs. Ground and dried SCGs were stirred in n-hexane to remove the major lipid, triacylglycerol. The pretreated SCGs were stirred in distilled water (DI water) containing TEMPO and NaBr. Oxidation was initiated by adding NaClO, and the mixture was stirred continuously for 3 h. The pH was maintained at 10-10.5 with either 0.5 M NaOH or 1 M HCl. The point at which the pH was stable for 10 min was considered the end-point, and the reaction was terminated by adding ethanol. The TEMPO-oxidized cellulose was vacuum-filtered, washed repeatedly with DI water, and then collected by freeze-drying. In this study, the properties of SCGs-derived TOCNFs were compared with those of the microcrystalline cellulose (MCC) derived from wooden materials. ^{13}C solid-state Nuclear Magnetic Resonance (^{13}C NMR) analysis confirmed the conversion of the -OH groups on the surface of the SCGs microfibers to carboxyl groups (-COOH) via TEMPO-mediated oxidation. XRD analysis indicated that SCGs-derived TOCNFs exhibited a lower crystalline structure compared to wood-derived MCC. This effect was attributed to the presence of residual hemicellulose, lignins, and triacylglycerols in the SCGs, which likely hinder the fibrillation process. Thermogravimetric analysis (TGA) revealed that SCGs-derived TOCNFs began to decompose at a markedly lower temperature (100°C) compared to MCC (280°C). Furthermore, differential thermogravimetry (DTG) revealed that TOCNFs underwent thermal degradation in two distinct stages. The first step observed at 251°C is attributed to the decomposition of thermally unstable sodium hydro-glucuronate units introduced during the oxidation process. The second step, observed at 267°C, is associated with the decomposition of unaltered cellulose chains. In contrast, MCC exhibited a single prominent degradation peak at 344°C. This variation might be due to the presence of anhydroglucuronate units in TOCNFs reduces the thermal stability of crystalline cellulose domains, leading to an earlier onset of decomposition. Khoshk & Moeenfard[19] prepared TEMPO-oxidized cellulose from SCGs with varying particle sizes, and their physicochemical properties were evaluated. Roasted *Robusta* coffee beans were powdered using a household grinder and sieved into three distinct size ranges: 850-1400, 500-850, and 355-500 μm. The powder was continuously stirred in DI water, followed by filtration and oven-drying to obtain the SCGs. The dried SCGs were defatted utilizing n-hexane in a Soxhlet apparatus, dispersed in 2 mol/L NaOH, and stirred at 90°C for 1 h. The solid residues were filtered, washed, and bleached with a 3% NaClO solution (v/v) at 90°C for 2 h. The bleached SCGs were suspended in DI water containing TEMPO and NaBr. TEMPO-mediated oxidation was initiated by adding NaClO at pH 10-10.5, and the reaction was terminated by adding absolute ethanol after the pH stabilized after 3 h of oxidation. The resulting TEMPO-oxidized cellulose was recovered by centrifugation and thoroughly washed, followed by dialysis in DI water at 4°C for 2 days. A 1.5% (w/v) TEMPO-oxidized cellulose suspension was then homogenized by ultrasonication using a disperser. The final TEMPO-oxidized cellulose product was freeze-dried and subsequently analyzed. Fourier transform infrared (FTIR) analysis confirmed that the TEMPO-oxidized cellulose exhibited a distinct C=O absorption peak that was absent in the original SCGs, indicating the formation of -COONa groups through oxidation. Morphological analysis employing scanning electron microscope (SEM) images revealed that the TEMPO-oxidized cellulose prepared from SCGs with particle sizes of 850-1400 μm formed a network-like structure composed of cellulose bundles. In contrast, TEMPO-oxidized cellulose derived from SCGs with particle sizes of 500-850 and 355-500 μm exhibited aggregated cellulose with irregularly shaped, short, and wide fibers. XRD showed that all TEMPO-oxidized cellulose exhibited a crystalline diffraction pattern characteristic of cellulose I. Among them, the TEMPO-oxidized cellulose derived from the 850-1400 μm SCGs fraction exhibited the highest crystallinity (49.9%), which was inversely proportional to the SCGs particle size. This trend may be attributed to a disruption of the crystalline regions within cellulose caused by TEMPO-mediated oxidation and mechanical disintegration. TGA results indicated a reduction in the thermal stability of TEMPO-oxidized cellulose with declining SCGs particle size. The TEMPO-oxidized cellulose prepared from SCGs with a particle size of 850-1400 μm demonstrated the maximal thermal stability, likely due to its greater crystallinity and longer fiber structure. Conversely, TEMPO-oxidized cellulose samples obtained from smaller-sized SCGs particles (500-850 and 355-500 μm) exhibited lower thermal stability, which may be associated with a reduction in the major crystalline domains and a relatively lower content of -COONa groups. Soni et al.[11] synthesized four types of cellulose nanofibers (CNFs) from cotton stalks using various chemical treatments such as H_2SO_4 hydrolysis and TEMPO-mediated oxidation, followed by ultrasonication. First, the ground cotton stalks were extracted with ethanol in a Soxhlet apparatus to remove the wax, and then dried. To extract pure cellulose, alkaline-acid pretreatment was used. The cotton stalks were soaked in a 15 wt% NaOH solution and then hydrolyzed with 1.0 M HCl at 80°C to dissolve the hemicelluloses. The fibers were then retreated with a 2.0 wt% NaOH solution and added with an acidified $NaClO_2$ solution at 75°C until the fibers turned completely white. These fully bleached fibers were then filtered and washed. CNFs were prepared from the pretreated cotton stalks by treating them with various chemicals. The H_2SO_4-neutralized CNFs were prepared by hydrolyzing the pretreated

cotton stalks with a 64% H_2SO_4 solution at 45°C for 50 min, followed by neutralization with a Na_2CO_3 solution and centrifugation. The H_2SO_4-dialyzed CNFs were prepared in the same manner, followed by dialysis in DI water for 4 days until the pH was neutralized. TOCNFs were prepared by suspending the pretreated cotton stalks in DI water, adding NaBr solution and TEMPO, and stirring for 10 min. The pH was maintained between 10 and 11 with 0.5 M NaOH, and 13% NaClO solution was added while stirring. After 1 h, ethanol was added to end the reaction, and 0.5 M HCl was used to adjust the pH to 7.0. The oxidized suspension was vacuum-filtered and washed with DI water. The H_2SO_4-neutralized CNFs, H_2SO_4-dialyzed CNFs, and TOCNFs were collected after ultrasonication followed by freeze-drying. In this study, the properties of the four different types of CNFs-untreated fully bleached pulp, H_2SO_4-neutralized CNFs, H_2SO_4-dialyzed CNFs, and TOCNFs—were compared. The chemical-ultrasonication treatment significantly affected the physiological properties of CNFs. Among these, TOCNFs formed more uniform and smaller nanofibers, due to the negative charges introduced by -COONa groups at the C6 position, which promoted electrostatic repulsion between fibers and their separation. FTIR analysis revealed that the TOCNFs exhibited a distinct C=O peak, distinguishing them from the other chemically treated CNFs. Moreover, TGA indicated that the TOCNFs underwent ~70% thermal degradation and began to decompose at a much lower temperature (215°C) compared to the H_2SO_4-neutralized CNFs (285°C) and H_2SO_4-dialyzed CNFs (225°C). This earlier onset of thermal degradation is attributed to the presence of -COONa groups formed during TEMPO-mediated oxidation. Pratama et al.[10] prepared CNFs from various cellulose sources, including corn cobs, bagasse, wood waste, and bacterial cellulose via TEMPO-mediated oxidation and evaluated their properties. Cellulose was isolated from lignocellulosic materials such as corn cobs, bagasse, and wood waste by grinding the raw material, followed by stirring the powder in 2% (w/v) NaOH at 80°C. The resulting precipitate was filtered and washed to remove the lignin and alkaline residues, and then dried in an oven at 60°C for 24 h. The dried powders were bleached using 1.7% (v/v) NaClO at 80°C, followed by filtration and washing with DI water. The white solid obtained was oven-dried at 60°C for 24 h, ground, and sieved through a 250 μm mesh. For bacterial cellulose, the gel obtained was processed in the same manner. The CNFs were separated using the TEMPO/NaBr/NaClO system. Cellulose sources (corn cobs, bagasse, wood waste, and bacterial cellulose) were dispersed in DI water containing TEMPO and NaBr. Oxidation was initiated by adding a NaClO solution. The pH was maintained at 10.5 by adding 0.5 M NaOH dropwise, and subsequently neutralized with 0.5 M HCl. The TOCNFs were recovered by vacuum filtration and washed with DI water. A 2% (w/w) suspension of the water-insoluble oxidized cellulose was prepared by adding DI water, followed by ultrasonication for 30 min. The same procedure was applied to MCC for comparison, and the TOCNFs characteristics were evaluated to assess the influence of diverse cellulose sources. FTIR spectroscopy was employed to analyze the cellulose molecular structure pre- and post-oxidation. A new peak appeared at 1740 cm^{-1} in the spectrum of oxidized cellulose, confirming the conversion of -OH groups to -COO^- groups. XRD analysis indicated that all samples exhibited peaks characteristic of cellulose I crystals diffraction at 2θ = 16°, 22.6°, and 34°. Notably, TOCNFs derived from MCC and bacterial cellulose were more crystalline than those from lignocellulosic biomass, attributed to the presence of amorphous regions composed of hemicellulose and lignin within the lignocellulosic biomass. The charge-indicative surface -COOH groups of TOCNFs obtained through TEMPO-mediated oxidation were measured. TOCNFs derived from MCC and bacterial cellulose exhibited higher surface charge than those derived from lignocellulosic biomass. In the case of MCC derived TOCNFs, this is attributed to residual sulfonate groups (SO_4^{2-}) remaining after acid hydrolysis during MCC production. However, TOCNFs derived from bacterial cellulose possess lacks sulfonate groups, resulting in lower surface charge compared to those from MCC. The surface -COOH groups of TOCNFs can influence suspension stability, interactions with other compounds, and dispersibility in various solvents. Hop et al.[12] also employed the TEMPO/NaBr/NaClO oxidation system to produce nanocellulose from bleached wood pulp. The pulp was stirred in DI water containing TEMPO and NaBr. Oxidation was initiated by slowly adding a NaClO solution, while maintaining the pH at 10, with 0.5 M NaOH. TEMPO-oxidized cellulose was filtered, thoroughly washed, and subsequently suspended in water to obtain a final concentration of 3% (w/v). The suspension was then ultrasonicated for varying durations to obtain the TOCNFs. FTIR analysis revealed a shift in the -OH bending-related vibration peak at 1630-1600 cm^{-1}, which indicated the conversion of the -OH groups at the C6 position to -COONa groups. XRD indicated the crystallinity values of pristine cellulose and TEMPO-oxidized cellulose to be 66% and 65.2%. This finding indicates that TEMPO-mediated oxidation selectively modified only the -OH groups to form -COOH groups, without affecting the cellulose crystalline structure. Under phase-contrast microscopy, the TEMPO-oxidized cellulose fibers appeared lighter than pure cellulose ones. This observation can be attributed to the negatively charged -COOH groups formed on the surface of TEMPO-oxidized cellulose, implying reduced interfacial interaction between the fibers due to charge repulsion. Fukuzumi et al.[20] also prepared TEMPO-oxidized cellulose from bleached softwood kraft pulp utilizing a TEMPO/NaBr/NaClO oxidation system and evaluated their properties. The pulp was suspended in DI water containing

TEMPO and NaBr. NaClO solution was added, and the suspension was stirred at room temperature and pH 10 until the consumption of 0.5 M NaOH stopped. To prevent unexpected reactions due to the -CHO groups generated during TEMPO oxidation, the oxidized cellulose was further treated with $NaClO_2$ in 0.5 M acetate buffer (pH 4-5) at room temperature for 24 h to remove these groups. The TEMPO-oxidized cellulose was then filtered, washed, and dispersed in DI water to obtain a solid content of 0.1%, followed by ultrasonication to synthesize the TOCNFs. According to the TGA analysis, the onset decomposition temperature of pristine cellulose was 275°C, whereas that of the TOCNFs decreased to 222°C. This reduction was ascribed to the transformation of the -CH_2OH groups at the C6 position to -COONa groups, which facilitated decarboxylation during thermal decomposition and weakened the molecular interactions, thereby accelerating degradation.

Previous studies have identified that TEMPO-mediated oxidation induces consistent and marked changes in the chemical structure, morphological characteristics, and physicochemical properties of cellulose. Chemically, TEMPO-mediated oxidation selectively converts the primary -OH groups at the C6 position of the cellulose backbone into -COONa or -COOH groups. The introduction of the negatively charged -COO^- groups imparts surface charge to the nanofibers, enhancing dispersibility and electrostatic repulsions between the individual fibers. Regarding morphological structure, TEMPO-mediated oxidation reduced the size of cellulose fibers to a nanoscale, resulting in uniform nanofibers. This phenomenon can be attributed to the introduction of surface charges during oxidation, which increases the electrostatic repulsion between fibers, thereby enhancing their susceptibility to subsequent mechanical treatments such as ultrasonication. TOCNFs typically exhibited the diffraction peaks typical of cellulose I crystals, and their crystallinity remained largely unchanged compared to that of pristine cellulose. This uniformity occurs because TEMPO-mediated oxidation selectively modifies only the primary -OH groups, converting them into -COONa or -COOH groups, without significantly affecting the cellulose crystalline structure. However, the TOCNFs derived from lignocellulosic biomass generally exhibited lower crystallinity than those from pristine cellulose or MCC, due to amorphous components of the raw biomass such as hemicellulose and lignin. In general, TOCNFs were less thermally stable compared to pristine cellulose. This finding may be attributed to oxidative degradation caused by the decarboxylation of -COONa groups that were formed during the TEMPO-mediated oxidation process, which weakened the cellulose molecular structure (Table 1).

2.3. Recent studies on physically blended TOCNFs films

To optimize the performance of TOCNFs films for potential applications in sustainable packaging materials, researchers have explored various physical blending strategies, including the preparation of monolayer films for coating, polymer-TOCNFs composite films, and plasticizers (Table 2).

To investigate the compatibility between polyvinyl alcohol (PVA) and the TOCNFs derived from SCGs, Kanai et al.[1)] prepared PVA/TOCNFs composite films by mixing a PVA solution with the TOCNFs derived from SCGs. A shift in the characteristic peaks, such as those of carbonyl and methyl groups, was observed when the TOCNFs were mixed with the PVA matrix. Additionally, TGA analysis revealed that the maximum decomposition temperature (289°C) of the PVA/TOCNFs composite film was between that of pure PVA (313°C) and TOCNFs films (255°C). This thermal behavior suggests H-bonding between the PVA matrix and TOCNFs. These results indicated that the TOCNFs derived from SCGs were successfully incorporated into the PVA matrix. Oh & Lee[21)] investigated the potential use of SCGs as packaging materials in the form of TEMPO-oxidized SCGs films prepared through delignification, TEMPO-mediated oxidation, and ultra-high pressure homogenization. Glycerol as a plasticizer, and 0.02 wt% cinnamaldehyde as a crosslinking agent, were used to improve the physical properties of the TEMPO-oxidized SCGs films. Film-forming solutions were obtained using ultra-high-pressure homogenization and subsequently cast to form monolayer films. An analysis of the resulting TEMPO-oxidized SCGs films showed that the addition of 1.5 wt% glycerol remarkably improved the mechanical properties, increasing tensile strength from 15.5 MPa to 23.3 MPa and elongation at break from 9.26% to 35.19%. This improvement may be attributed to glycerol acting as a plasticizer that disrupts the intermolecular hydrogen bonding within the cellulose network. Soni et al.[22)] developed transparent and high-performance bio-nanocomposite films by incorporating TOCNFs into a chitosan matrix as reinforcing agents. In this study, chitosan, TOCNFs, and sorbitol were dispersed in a 2% acetic acid solution, and the mixture was dried in petri dishes to form films. The TOCNFs composition varied at 0%, 5%, 10%, 15%, 20%, and 25%, while the sorbitol ratio was fixed at 25%. Morphological examinations confirmed the uniform dispersion of the TOCNFs within the chitosan matrix. As the TOCNFs concentration within the chitosan matrix increased, the surface of the composite films slightly roughened. In addition, the mechanical properties were improved due to robust electrostatic interactions between the TOCNFs and chitosan. As the water absorption rate, water vapor, and oxygen permeability decreased, the absorption and permeation of the gas molecules into the composite matrix became difficult. This phenomenon can be due to the electrostatic repulsions between the negatively charged TOCNFs and the positively charged chitosan.

Table 1. Summary of the previous research findings on TEMPO-mediated oxidation and its impact on the properties of cellulose derived from diverse natural sources

Cellulose source	Characterization and properties	Major findings	Ref.
SCGs	Chemical structure	• ^{13}C NMR analysis confirmed the conversion of the surface -OH groups of SCGs microfibers to -COOH groups via TEMPO-mediated oxidation.	(Kanai et al., 2020)
	Morphological structure	• XRD analysis showed that the crystallinity of the TOCNFs derived from SCGs (72%) was lower than that from the MCC (79%).	
	Thermal properties	• The main degradation temperatures of SCGs-derived TOCNFs were observed at 251°C and 267°C, which are significantly lower than that of MCC (344°C), indicating reduced thermal stability of the SCGs-derived TOCNFs.	
SCGs	Chemical structure	• FTIR analysis exhibited a distinct C=O peak at 1610 cm^{-1} in TEMPO-oxidized cellulose, indicating the successful formation of -COONa groups through TEMPO-mediated oxidation.	(Khoshk, & Moeenfard, 2025)
	Morphological structure	• SEM analysis indicated that the SCGs particle size was affected by TEMPO-oxidized cellulose morphology, with larger particles forming networks and smaller particles producing irregular, aggregated fibers. • XRD analysis revealed that TEMPO-oxidized cellulose retained the cellulose I structure; the highest crystallinity was observed in larger SCGs particles (49.2%), and it decreased with smaller particles (37.2%).	
	Thermal properties	• The thermal stability of SCGs-derived TEMPO-oxidized cellulose was directly proportional to the SCGs particle size. TEMPO-oxidized cellulose derived from SCGs with larger particle size showed higher thermal degradation temperatures (290°C and 404°C), while samples from smaller particles exhibited lower values (246-250°C and 353-365°C).	
Cotton stalks	Chemical structure	• FTIR analysis of the TOCNFs showed a distinct absorption peak at 1610 cm^{-1}, corresponding to the -COONa groups introduced at the C6 position.	(Soni, Hassan, & Mahmoud, 2015)
	Morphological structure	• Negatively charged -COONa groups at the C6 position enhanced the electrostatic repulsion between fibers, promoting separation, uniformity, and smaller TOCNFs.	
	Thermal properties	• The decomposition temperature of TOCNFs was observed at 215°C, which is lower than that of H_2SO_4-dialyzed CNFs (225°C), indicating reduced thermal stability of TOCNFs due to the formation of -COONa groups during the TEMPO-mediated oxidation process.	
Corn cobs Bagasse Wood waste Bacterial cellulose	Chemical structure	• FTIR analysis exhibited that the -OH groups on the TOCNFs were converted to $-COO^-$ groups through TEMPO-mediated oxidation, resulting in the appearance of a new characteristic peak at 1740 cm^{-1}.	(Pratama et al., 2024)
	Morphological structure	• XRD analysis of TOCNFs exhibited characteristic cellulose I crystalline diffraction peaks. TOCNFs derived from MCC (83%) and bacterial cellulose (82%) showed enhanced crystallinity compared to those derived from lignocellulosic biomass (73%-78%).	
Bleached wood pulp	Chemical structure	• FTIR analysis confirmed the conversion of the -OH groups at the C6 position to -COONa groups, as evidenced by the shift of the absorption peak from 1630 cm^{-1} to 1600 cm^{-1} corresponding to the asymmetric stretching of carboxylate groups.	(Hop et al., 2022)
	Morphological structure	• XRD analysis indicated that the crystallinity of TEMPO-oxidized cellulose (65.2%) did not differ significantly from that of pristine cellulose (66%). • Phase-contrast microscopy revealed that the TEMPO-oxidized cellulose fibers appeared brighter than pristine cellulose fibers.	
Bleached softwood kraft pulp	Thermal properties	• The thermal decomposition temperature of TOCNFs was 222°C, which is lower than that of pristine cellulose at 275°C. This decrease in thermal stability is attributed to the presence of -COONa groups formed during TEMPO-mediated oxidation.	(Fukuzumi, Saito, Okita, & Isogai, 2010)

Table 2. Summary of the recent research on physically blended TOCNFs films

Cellulosic source	Product	Preparation method	Major findings	Ref.
SCGs	PVA/TOCNFs composite films	Casting	• The characteristic peaks (carbonyl and methyl groups) shifted upon mixing TOCNFs with the PVA matrix. • The thermal stability was enhanced with a maximum decomposition temperature (289°C) between those of pure PVA (313°C) and TOCNFs films (255°C), indicating H-bonding.	(Kanai et al., 2020)
SCGs	TEMPO-oxidized SCGs-based monolayer films	Solvent casting, Vacuum filtration	• The mechanical properties were improved with the addition of 1.5 wt% glycerol as a plasticizer.	(Khoshk & Moeenfard, 2025)
Cotton stalks	Chitosan/ TOCNFs composite films	Casting	• The tensile strength and Young's modulus were enhanced by increasing the TOCNFs contents (0%, 5%, 10%, 15%, 20%, and 25%) within the chitosan matrix. • The water vapor and oxygen barrier properties were improved by increasing the TOCNFs contents (0%, 5%, 10%, 15%, 20%, and 25%) within the chitosan matrix.	(Soni et al., 2016)

3. Recent studies on RC films

RC films with better biodegradability, renewability, and recyclability have gained significant attention in recent years due to their remarkable potential in a wide range of applications[6,14,15,23,24]. Owing to their excellent mechanical, optical, and gas barrier properties, RC films are increasingly being use in various industries, including textiles, energy, pulp and paper, pharmaceuticals, and packaging films[6,14,23,24].

The preparation of RC films typically involves two key steps: the dissolution of cellulose in an appropriate organic solvent, followed by regeneration in a coagulation bath[23,24]. Various solvent systems, including aqueous alkali, phosphoric acid, amine oxides, and ionic liquids, have been employed for dissolving cellulose. Among these, the sodium hydroxide/carbon disulfide ($NaOH/CS_2$) system, used in viscose rayon and cellophane production, is effective but environmentally hazardous, as CS_2 is toxic and generates harmful wastes. Similarly, NMMO enables cellulose dissolution at high temperatures (>85°C), but suffers from side reactions, instability, and by-product formation[6,8,24,25]. These challenges necessitate the development of safer and more efficient solvent systems.

3.1. Dissolution mechanism of cellulose in the DMAc/LiCl system

DMAc/LiCl is one of the most extensively studied cellulose solvent systems due to its high polarity, thermal stability, and ability to dissolve without structural degradation. Unlike other ionic liquids, it does not require additives or specialized equipment and offers excellent recyclability[6,15,24,26]. In this system, LiCl exists as dissociated Li^+ and Cl^- ions[8], as shown in Fig. 2. The Cl^- anions form H-bonds with the -OH groups of cellulose, thereby disrupting their interactions with other groups, and replacing the existing OH-OH-bonds with OH-Cl^- ones. Additionally, Li^+ ions form a $Li^+(DMAc)_x$ cationic complex by interacting with the carbonyl oxygen (C=O) of the DMAc molecules, facilitating the dissolution of cellulose[8,26,27]. McCormick et al.[27] reported that when cellulose dissolves in the DMAc/LiCl system, the $Li^+(DMAc)_x$ cationic complex binds with Cl^- ions, and the Li^+ ions do not interact directly with the -OH groups of the cellulose molecules. Thus, Li^+ ions

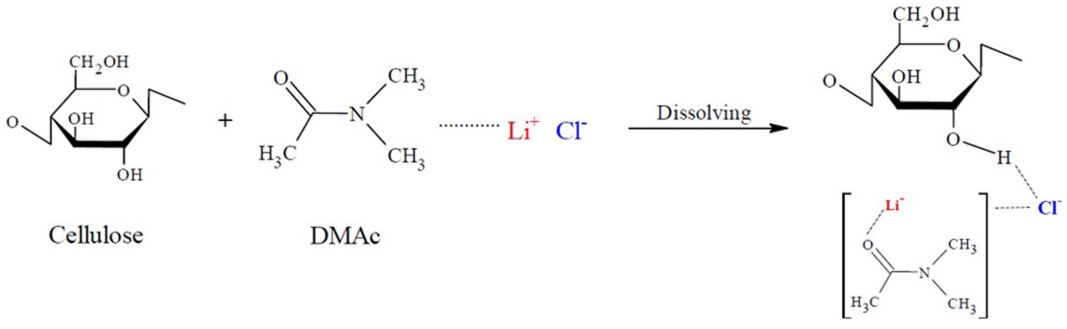

Fig. 2. Dissolution mechanism of cellulose in DMAc/LiCl solvent[8,26,27].

mainly play a role in maintaining the stability of the solvent system without direct interactions with cellulose.

Zhang et al.[8] reported that when cellulose dissolves in the DMAc/LiCl cosolvent system, H-bonds are formed between the protons of the cellulose -OH groups and Cl^- ions. During this process, the H-bonding network between cellulose molecules is broken, and LiCl dissociates into Li^+ and Cl^- ions. Subsequently, the Li^+ ions are further solvated by the free DMAc molecules, and these ions form an electrostatic equilibrium with the Cl^- ions that are H-bonded to the cellulose molecules. This rearrangement allows the cellulose chains to disperse within the solvent system and form a homogeneous solution.

Wang et al.[26] investigated the dissolution mechanism of cotton-derived MCC in the DMAc/LiCl system by employing a pretreatment step involving the prolonged soaking of MCC in either water or DMAc. This pretreatment induced the delamination of cellulose particles, facilitating the formation of nanopores on the cellulose surface, which markedly enhanced the diffusion of Cl^- ions into the cellulose matrix. The Cl^- ions formed H-bonds with the -OH groups of cellulose and generated the electrostatic repulsion between chains. This phenomenon disrupted the intermolecular H-bonds and peeled off the external cellulose layers. This synergistic effect ultimately enabled the complete dissolution of cellulose in the DMAc/LiCl solvent system. This process is highly dependent on various parameters, such as temperature, the DMAc/LiCl ratio, and coagulation conditions, which influence the viscosity and stability of the RC solution; their optimization is essential for producing high-quality RC films.

3.2. Recent studies on the development of RC film from food by-product biomass

Several recent studies have explored the preparation and characterization of RC films from various biomass sources for use in sustainable packaging, including biodegradable, active, and intelligent packaging systems (Table 3).

Zhao et al.[5] extracted cellulose from durian peels using the DMAc/LiCl solvent system to develop biodegradable packaging materials. After mechanically grinding the peels, hemicellulose and lignin were extracted with alkaline and bleaching solutions, and cellulose via acid treatment. The extracted cellulose was swollen by stirring in water, immersed in methanol and DMAc to prevent H-bond reformation, and then dissolved completely in a DMAc/LiCl solution. The prepared cellulose solution was cast onto a glass plate, regenerated with water, and dried to form a transparent RC film (DC film). XRD and FTIR confirmed that the chemical structure of cellulose extracted from durian peels closely resembled that of commercial cellulose derived from cotton linters. Morphological analysis revealed that the DC film had a smooth and homogeneous surface and a cross-section similar to commercial cellulose (CC) film and cellophane. TGA results indicated that the DC film was more thermally stable compared to the CC film. The CC film exhibited an initial weight loss at ~150°C. However, the thermal degradation of the DC film began at ~270°C, with two distinct stages at ~270 and 345°C due to the decomposition of the cellulose matrix and salts, respectively. Notably, the char residue of the DC film was remarkably lower than cellophane film at 480°C, suggesting high levels of additives in the latter. An examination of the mechanical properties showed that the elongation at break of DC and CC films was ~6% and 8%, much lower than cellophane film (35%). This variation might be due to the inclusion of a plasticizer in cellophane film. Biodegradability was assessed through a 4-week-long soil burial test. Compared with cellophane and DC film, the RC film exhibited a faster biodegradation rate in the soil during the first two weeks and complete degradation at 4 weeks.

Saedi et al.[3] extracted cellulose from ginger pulp through mechanical and chemical treatments, including grinding, dewaxing, alkali treatment, bleaching, and acid hydrolysis. Initially, 3 g of the extracted cellulose was dispersed in 150 mL of distilled water, followed by redispersion in methanol. Subsequently, the cellulose was filtered and dissolved in a DMAc/LiCl solvent system while stirring for 12 h. The cellulose solution obtained was centrifuged at 5°C for 10 min to remove the air bubbles and then cast onto a Teflon-coated glass plate. The plate was gently immersed in different coagulation baths (water, ethanol, or acetone) to obtain an RC gel. The gel was then immersed overnight in a 3% (v/v) water-glycerol solution to remove any remaining solvent. The gel was spread on a Teflon-coated glass plate and fixed by drying overnight at room temperature to obtain the RC film. Morphological studies revealed that the RC films obtained from the ethanol or acetone coagulation baths exhibited smooth surfaces, whereas those from the water coagulation bath showed rough surfaces. This variation can be attributed to differences in phase inversion rates between the DMAc/LiCl solvent system and coagulation solvents such as water, ethanol, and acetone. The high mixing rate between the DMAc/LiCl solvent system and water leads to immediate phase inversion and coagulation on the surface of the cellulose solution. As a result, the RC chains do not have sufficient time to align and form a dense, uniform structure, resulting in a rough film morphology. In contrast, the slower solvent exchange with organic solvents such as ethanol or acetone allows more time for RC chain rearrangement, promoting the formation of smoother and more dense film surfaces. Mechanical property analyses showed that the RC films obtained from the ethanol and water coagulation baths had the maximum and lowest mechanical strengths of 51.4 ± 5.9 and 29.5 ± 2.4 MPa, respectively. SEM indicated that the RC film prepared using water as the coagulating agent contained numerous pores, which disrupted

Table 3. Summary of the recent research findings on the properties and potential applications of RC film

Cellulosic source	Dissolution Solvent System	Regeneration Method	Major findings	Ref.
Durian peels	DMAc/LiCl	DI. Water	• The durian peels based RC (DC) film exhibited enhanced thermal stability, with thermal degradation starting at 270°C compared to 150°C for commercial cellulose (CC) film. • The DC film showed a smooth and homogeneous morphology with similar cross-sectional structure to cellophane. • Biodegradability was significantly improved, with complete degradation observed within 4 weeks during a soil burial test.	(Zhao et al., 2019)
Ginger pulp	DMAc/LiCl	DI. Water, Ethanol, Acetone	• The mechanical strength varied significantly depending on the coagulation solvent, with ethanol-based films achieving the highest tensile strength (51.4 ± 5.9 MPa) and water-based films the lowest (29.5 ± 2.4 MPa). • Composite RC films incorporating 3% ZnO nanoparticles and 1% curcumin (RC/ZC) exhibited enhanced antimicrobial and antioxidant activity against multiple foodborne pathogens.	(Saedi et al., 2023)
Borassus fruit fiber	AmimCl	DI. Water	• XRD analysis indicated a transition from crystalline cellulose I in raw fibers to predominantly amorphous cellulose in the RC film. • The RC film demonstrated high mechanical performance with a tensile strength of 111 MPa and an elastic modulus of 6149 MPa.	(Reddy et al., 2017)

inter-chain bonding, significantly reducing its ability to transmit and withstand mechanical stress. To provide active antimicrobial and antioxidant functionality to the RC films, Saedi et al.[3] further developed RC/zinc oxide-curcumin (RC/ZC) composite films. To prepare these composite films, 3% ZnO NPs and 1% curcumin were dispersed in a DMAc/LiCl solution and homogenized utilizing ultrasonication. The prepared mixture was then added to a cellulose solution to obtain the RC film. Compared to the RC film, the RC/ZC composite film showed decreased tensile strength and Young's modulus, but an increased elongation at break. This variation was attributed to a reduction in H-bonding between the polymer chains caused by the incorporation of curcumin and ZnO NPs. Furthermore, the RC/ZC composite film exhibited antimicrobial and antioxidant activities against various foodborne pathogenic bacteria, including *Listeria monocytogenes*, *Staphylococcus aureus*, *Bacillus cereus*, *Escherichia coli*, *Salmonella typhimurium*, and *Vibrio parahaemolyticus*.

Reddy et al.[6] dissolved the cellulose extracted from borassus fruit fibers in an ionic 1-allyl-3-methylimidazolium chloride liquid (AmimCl) to obtain the RC films. Cellulose extraction involved delignification with a toluene-ethanol mixture, followed by a NaClO solution at 100°C, and hemicellulose removal via NaOH treatment. The extracted cellulose was dissolved in AmimCl at 80°C for 120 min, and cast onto a glass plate to form a film. The film was coagulated, washed with DI water to remove the ionic liquid, and then dried to obtain the final RC film. Morphological analysis of the RC film made from borassus fruit fibers exhibited a smooth surface and compact cross-sectional structure, indicating a higher level of molecular alignment during the regeneration process. XRD analysis of the RC film showed that the characteristic diffraction peaks of cellulose I in the raw fibers transformed into those of cellulose II in the extracted cellulose; these peaks almost disappeared in the RC film, where amorphous cellulose predominated. Additionally, a broad peak at $2\theta = 19.6°$ confirmed the presence of residual cellulose II in the RC film. The crystallinity indices of the raw fibers, extracted cellulose, and RC film were 45.5%, 66.6%, and 41%, respectively. The decreased crystallinity in the RC film can be attributed to the disruption of H-bonds during the dissolution and regeneration of the cellulose extracted from the borassus fruit fibers. TGA showed that the maximum decomposition temperatures were 379°C, 394°C, and 368°C for the raw fibers, extracted cellulose, and the RC film, respectively. This decline in the thermal stability of the RC film was attributed to a greater disruption of the inter- and intra-molecular H-bonds during dissolution compared to the raw borassus fibers or the extracted cellulose. The RC film made from borassus cellulose exhibited a high tensile strength (111 MPa) and elastic modulus (6,149 MPa), demonstrating superior properties compared to commercially available polyolefin films (PP and PE).

4. Conclusion

The growing concern over environmental issues, the demand for sustainable materials has been increasing. Cellulose-based biomass derived from renewable resources such as agricultural, marine, and food processing wastes is considered a promising alternative to non-renewable resources due to its biodegradability and sustainability. Consequently,

extensive research efforts have been dedicated to valorizing food by-products and waste into high-value materials. This review investigates the principles and mechanisms of TEMPO-mediated oxidation, the characteristics of TOCNFs and their applications, the main solvent systems and dissolution mechanisms of cellulose, as well as the properties and utilization of RC films. Previous studies have extensively demonstrated the fabrication of TOCNFs and TOCNFs composite films via TEMPO-mediated oxidation from various biomass resources, evaluations of their physicochemical properties. Characterization of TOCNFs has confirmed their high aspect ratio, abundant functional groups (-COONa), and excellent thermal stability. Furthermore, TOCNFs composite films exhibit superior mechanical strength, thermal properties, and oxygen barrier performance. Recent research has reported that RC films exhibit excellent biodegradability, renewability, and mechanical properties, indicating their high potential as eco-friendly packaging materials. Especially, the DMAc/LiCl solvent system has attracted attention as a promising solvent due to its effective cellulose dissolution capability while minimizing structural damage. Extensive studies have been conducted on the fabrication and property evaluation of RC films derived from various food by-products. These films have demonstrated thermal stability, crystallinity, and mechanical strength comparable to or exceeding those of commercial cellulose films. TOCNFs and RC films are recognized as promising sustainable materials with diverse potential applications. The complementary properties of these materials provide opportunities for the development of multilayer films through a layer-by-layer coating approach. However, there are still some challenges that limit industrial applications. Future research and technological development should focus on the large scale production of high-quality materials, enhancement of functional properties, design integration with food products, cost-effectiveness, and comprehensive safety assessments.

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