Advances in the chemical modification of nanocellulose for biodegradable plastics reinforcement

Shuya Zhang[1], Mingda Che[2*], Renliang Huang[3,4*], Mei Cui[1], Wei Qi[1], Rongxin Su[1,2,3]
(1. *State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China*;
2. *Ningbo Key Laboratory of Green Petrochemical Carbon Emission Reduction Technology and Equipment, Zhejiang Institute of Tianjin University, Ningbo 315201, Zhejiang, China*;
3. *Tianjin Key Laboratory for Marine Environmental Research and Service, School of Marine Science and Technology, Tianjin University, Tianjin 300072, China*;
4. *Tianjin Sustainable Novel Materials Co. Ltd., Tianjin 300192, China*)

Abstract: As non-degradable traditional plastics contribute to environmental pollution, biodegradable polymers have been identified as a promising alternative. However, inherent drawbacks such as low toughness, poor tensile strength, and reduced thermal degradation temperatures limit the further development of biodegradable polymers. Nanocellulose has the potential to enhance the properties of biodegradable polymers without compromising their biodegradability. However, the abundant hydroxyl groups in nanocellulose's molecular chains result in poor compatibility with hydrophobic polymers, requiring surface modification prior to their combination. This review first introduces several common biodegradable polymers and three types of nanocellulose, followed by a comprehensive analysis of the recent advancements in the chemical modification methods of nanocellulose over the last five years. These methods encompass esterification, oxidation, silylation, and graft modification. The focus of this discussion is primarily on the modification strategies, enhancement effects, and mechanisms. Furthermore, the degradability and applications of modified nanocellulose composites are summarized. Finally, the main challenges hindering the development of chemically modified nanocellulose-reinforced biodegradable polymers are proposed. It is hoped that this review will inspire future researchers to develop industrially valuable chemically modified nanocellulose-reinforced biodegradable polymers.

Keywords: biodegradable polymers, nanocellulose, surface modification, reinforcement mechanisms, degradability, application
DOI: 10.25165/j.ijabe.20251801.9479

Citation: Zhang S Y, Che M D, Huang R L, Cui M, Qi W, Su R X. Advances in the chemical modification of nanocellulose for biodegradable plastics reinforcement. Int J Agric & Biol Eng, 2025; 18(1): 10–24.

1 Introduction

Non-degradable petroleum-based plastics have caused substantial environmental pollution issues, driving the development of bioplastics as a sustainable solution[1,2]. Bioplastics are categorized into three types: biobased and biodegradable [e.g., polylactic acid (PLA) and polyhydroxyalkanoates (PHA)], partly or fully biobased but non-degradable [e.g., bio-polyethylene (PE), bio-polyamide (PA), and bio-polyethylene terephthalate (PET)], and petroleum-based but biodegradable [e.g., polycaprolactone (PCL), polybutylene succinate (PBS), and polybutylene adipate terephthalate (PBAT)]. Among these, bio-based and non-biodegradable composites hold significant potential in automotive manufacturing, while biodegradable composites are more suitable for sustainable packaging[3]. Despite industrial-scale production of some bioplastics, several controversial issues and inherent performance limitations persist. First, the central issue with biodegradable plastics lies in their actual biodegradability[4]. Many biodegradable plastics require specific conditions, such as high temperatures, high humidity, or the presence of microorganisms, to degrade effectively, and often do not degrade quickly in the natural environment. In marine environments, where fungi populations are relatively low, many biodegradable plastics degrade at rates similar to non-biodegradable plastics, posing an urgent challenge[5]. Furthermore, replacing standard plastics with bio-based and biodegradable alternatives is insufficient unless they also exhibit comparable performance and cost-effectiveness. However, bioplastics still require advancements in mechanical properties, heat resistance, and cost-effectiveness. For instance, the tensile strength of PBAT (20-30 MPa) is approximately half that of conventional plastics, while the thermal deformation temperature of PHA ranges from 50°C to 60°C, which is significantly lower than that of commonly used traditional plastics. The performance stability of PLA in wet environments is inferior to that of polyethylene (PE), which is almost non-absorbent. In addition, PLA products exhibit

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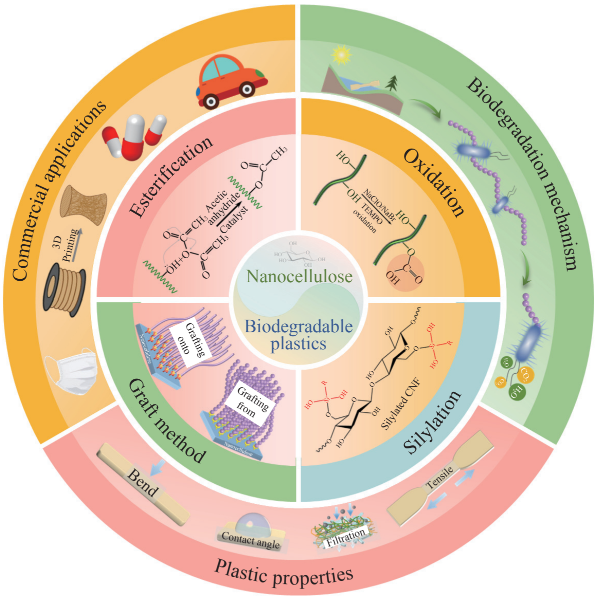
Received date: 2024-10-30 **Accepted date:** 2024-12-05

Biographies: Shuya Zhang, MS candidate, research interest: nanocellulose, biodegradable plastics and composites, Email: zsy_1005@tju.edu.cn; **Mei Cui**: Associate researcher, research interest: food preservation, preparation and application of nanocellulose, Email: meicui@tju.edu.cn; **Wei Qi**: Professor, research interest: enzyme engineering and biocatalysis, bioenergy and biobased chemicals, Email: qiwei@tju.edu.cn; **Rongxin Su**, Professor, research interest: Sustainable biological nanomaterials, comprehensive utilization of seawater resources, Email: surx@tju.edu.cn.
***Corresponding author: Mingda Che**, Post-doctor fellow, research interest: plastic reinforcement. Ningbo Key Laboratory of Green Petrochemical Carbon Emission Reduction Technology and Equipment, Zhejiang Institute of Tianjin University, Ningbo 315201, Zhejiang, China. Tel: +86-022-27407799, Email: cmd@tju.edu.cn; **Renliang Huang**, Professor, research interest: preparation and application of nanocellulose/chitin, solar desalination and resource utilization. Tianjin Key Laboratory for Marine Environmental Research and Service, School of Marine Science and Technology, Tianjin University, Tianjin 300072, China. Tel: +86-022-27407799, Email: tjuhrl@tju.edu.cn.

drawbacks, including low oxygen barrier properties and poor toughness[6]. On the other hand, the cost of PHA is significantly higher, nearly double that of PLA[7]. The mechanical properties of other bioplastics are generally inferior to conventional petroleum-based polymers[8]. Therefore, to overcome application limitation and advance the development of these bioplastics, their performance must be improved at a competitive cost. The incorporation of nanofillers, such as graphene, titanium dioxide, calcium carbonate, and biopolymers, into the bioplastic matrix appears to be a promising strategy[9,10]. Among these strategies, combining bioplastics with biopolymers has proven effective in enhancing properties without compromising biodegradability. Cellulose, the most abundant biopolymer, has been widely used as the component, filler, or processing additive in bioplastic composites[11]. These composites are recognized as being more environmentally friendly, cost-effective, and lightweight compared to traditional aramid, glass fibers, and talc-filled composites[3]. However, composites directly reinforced with cellulose exhibit unsatisfactory properties. Fortunately, advances of nanotechnology have introduced nanocellulose, unlocking new possibilities for improving the performance of bioplastic composites. Nanocellulose, a nanoparticle typically derived from cellulose, has a semi-crystalline nature and a hierarchical structure with at least one dimension in the nanometer range (1-100 nm)[12]. Nanocellulose can be extracted through various methods, including chemical, mechanical, and bacterial approaches[11]. Based on size, morphology, and preparation method, nanocellulose can be classified into three types: cellulose nanocrystals (CNC), cellulose nanofibrils (CNF), and bacterial nanocellulose (BNC)[13]. Researchers have used various types of nanocellulose to reinforce a wide range of composites, including bio-based materials. Nanocellulose can improve both the mechanical and thermal properties of bioplastics while also enhancing their overall biodegradation rate. For instance, the degradation rate of PLA is 0.5%/h, whereas the degradation rate of nanocellulose/PLA composites increases to 0.8%/h[14]. Sustainable biocomposites composed of bioplastics and advanced green nanocellulose demonstrate significant potential in aerospace, automotive parts manufacturing, packaging, and other industries[15]. However, the adoption of nanocellulose-reinforced biocomposites in various applications depends on several key factors, including structural stability, flame resistance, moisture resistance, and barrier properties[3].

Nanocellulose combines high strength, stiffness, toughness, and large aspect ratios due to its intricate architecture, while maintaining the non-toxic, biodegradable, renewable, and tunable surface chemistry properties of cellulose[16,17]. Additionally, it retains the natural hydrophilicity of cellulose due to the abundance of hydroxyl groups on its molecular chain[18]. Thus, there are two significant drawbacks to reinforcing the hydrophobic matrix with nanocellulose. First, the poor compatibility between the hydrophilic nanocellulose and the hydrophobic matrix leads to weak interfacial adhesion between them. Second, nanocellulose tends to aggregate within the matrix instead of disperse uniformly. The synergistic effects of these two issues can disrupt stress transfer, whereas effective stress transfer is critical in determining the overall mechanical properties of composites[19]. The importance of the processing method on the properties of the final composites cannot be ignored. Commercially used nanocellulose for bioplastic reinforcement is typically negatively charged, such as those prepared via sulfuric acid or 2,2,6,6-tetramethylpiperidinyloxyl radical (TEMPO)/bleach oxidation methods. This negatively charged nanocellulose disperses more effectively in polar solvents, facilitating the development of solvent casting for preparing nanocellulose biocomposites[20]. Other commonly employed processing methods include extrusion, hot pressing, and 3D printing (additive manufacturing)[3].

Besides choosing appropriate processing methods to improve composites properties, another prominent approach is the surface modification of cellulose. This involves introducing hydrophobic groups onto the cellulose surface to enhance the compatibility of nanocellulose with hydrophobic matrices. While several reviews offer comprehensive summaries of surface modification[11,21] and interfacial engineering[22], most of these have focused primarily on the combination of petroleum-based polymers with nanocellulose. At present, reviews on nanocellulose-reinforced bioplastics have centered primarily on PLA[9,10], with insufficient coverage on the reinforcement of other matrices. This review highlights the use of nanocellulose to reinforce a wide range of bioplastic matrices. It provides a comprehensive summary of the modification strategies employed in the preparation of nanocellulose biocomposites and their effects on composite properties. Furthermore, while numerous studies have investigated the impact of nanocellulose on the degradability of biocomposites, comprehensive reviews in this area reveal a noticeable gap which this paper aims to address. Finally, based on the current modification strategies and product applications, this review highlights some issues and challenges that still require further attention and improvement (Figure 1). This article aims to provide a fresh perspective and a comprehensive overview for researchers in the field.



Note: Including surface modification methods of nanocellulose, plastic properties, biodegradation mechanism, and commercial applications for degradable plastics, as summarized in the present review.

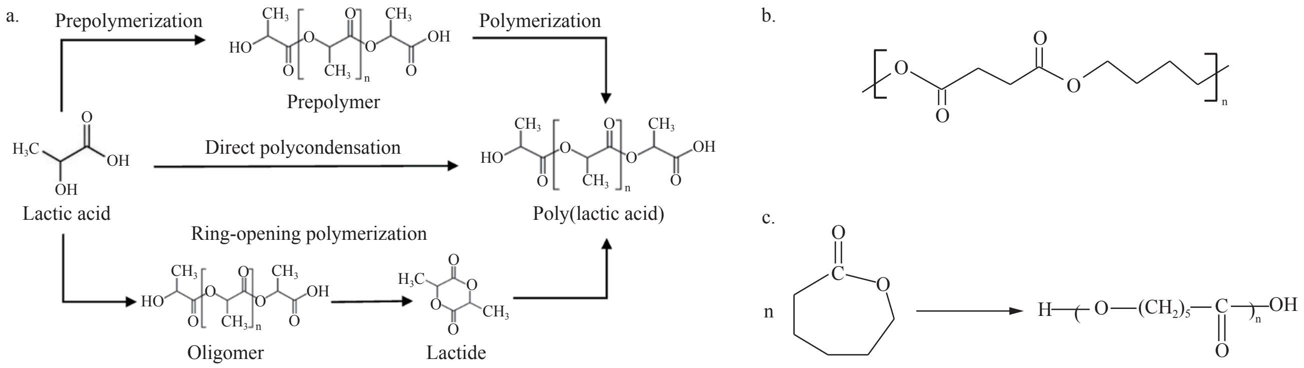
Figure 1 Schematic organization of the main contents

2 Biodegradable polymers

As mentioned above, bioplastics made from both naturally occurring and chemically produced materials, sourced from renewable or petroleum-based resources, are typically categorized into three main types: biobased and biodegradable, petroleum-based but biodegradable, and partly or fully biobased but nondegradable[23]. This article focuses on the first two types of degradable polymers, collectively referred to as biodegradable polymers (or biodegradable plastics). Biodegradable polymers, as the name implies, are inherently degradable polymers in nature that consist of chain-like molecules made up of covalently bonded monomer units. These polymers are designed to minimize environmental impact by promoting sustainability and reducing waste in comparison to traditional petroleum-based polymers. In fact, biodegradable polymers can be categorized into various types, including polysaccharides, polypeptides (proteins), and lipids. These classifications can be based on different criteria such as their sources, synthesis methods, and chemical compositions. However, since there are already comprehensive reviews that provide an in-depth overview[24,25], this section will focus specifically on biobased biodegradable polymers and petroleum-based biodegradable polymers.

2.1 PLA

Biobased biodegradable polymers are polymers derived from renewable biological resources and capable of breaking down into natural substances through biological processes, such as microbial action. Among these, the most common is PLA, a linear aliphatic semicrystalline polyester known for its versatility and excellent barrier properties. As a result, PLA is increasingly considered as a sustainable alternative to polypropylene (PP) and polystyrene (PS) in packaging and other demanding applications[26]. As illustrated in Figure 2a, the synthesis of PLA typically involves three main routes: two-step polymerization, direct polycondensation, and ring-opening prepolymerization[27].



Note: a. Routes of PLA synthesis from lactic acid[27]; b. chemical structure of PBS[28]; c. ring-opening polymerization of ε-caprolactone[29].

Figure 2 Monomer structure and synthesis of biodegradable polymers

However, several drawbacks of PLA limit its broader application, including a low crystallization rate, poor heat resistance, and brittleness[30]. Numerous methods have been developed to improve the performance of PLA, including the incorporation of inorganic and organic materials, as well as copolymerization and blending with various flexible polymers. In comparison to PLA products mixed with organic substances like N, N-ethylenebis (12-hydroxystearamide) (EBSA) and N,N-ethylenebis (stearamide) (EBH)[31], the addition of inorganic materials such as montmorillonite, calcium carbonate, and natural cellulose fiber generally enhances the rigidity and toughness of PLA products, while reducing ductility and tensile strength[10]. Additionally, achieving a balance between the degradability and mechanical properties of PLA blends presents a significant challenge.

The toughening agents used in PLA are typically non-degradable. Although some degradable toughening agents have been developed, their incorporation often leads to a decrease in the strength and modulus of PLA. This highlights the challenge of achieving a balance between degradability and mechanical properties in PLA blends.

2.2 PHA

PHA is a polyester that is naturally produced and stored as granules in many Gram-negative and Gram-positive bacteria[32]. Most PHA is linear polyesters composed of 3-hydroxy fatty acid monomers. There are various PHA monomer structures, allowing for the design of PHA polymers with differing levels of transparency, flexibility, and strength to meet specific needs. These versatile polymers can be applied across multiple fields, including packaging and agriculture. Furthermore, the non-toxicity, biocompatibility, and antibacterial properties of PHA broaden its applications in the medical field. They are anticipated to serve as a sustainable alternative to traditional plastics, such as PE and polypropylene PP. However, compared to PLA and other plastic substrates, the synthesis cost of PHA is significantly higher, posing a considerable challenge for achieving low-cost industrial production of PHA.

Poly (3-hydroxybutyrate) (PHB) is the most representative type in the PHA polymer family. PHB can be produced from various biomass feedstocks, including lignocellulosic waste, dairy industry waste, oil industry waste, starchy substrates, and sucrose-based substrates[33]. Due to its excellent oxygen permeability and UV resistance, PHB has the potential for widespread application in packaging films, drug release, wound dressings, and bone replacements. In addition to PHB, poly-3-hydroxybutyrate-*co*-poly-3-hydroxyvalerate (PHB/PHV or PHBV) is another commonly studied short-chain PHA, which is a copolymer of PHB and poly (3-hydroxyvalerate) (PHV). However, both PHB and PHBV often exhibit relatively stiff and brittle properties.

2.3 PBS

Petroleum-based biodegradable polymers are polymers derived from petrochemical raw materials that can be degraded by microorganisms under specific conditions. These polymers are of significant interest due to their similar physical and chemical properties to traditional plastics, alongside their ability to biodegrade after use.

PBS can be prepared from polycondensation of 1,4 butanediol with aliphatic dicarboxylic acid succinic acid[34]. The chemical structure of PBS is shown in Figure 2b[28]. PBS has attracted much attention because of its good flexibility, chemical resistance, impact strength, and reasonable cost. In particular, PBS offers excellent processing versatility due to its glass transition temperature, which is below room temperature. This property enables a wide range of manufacturing techniques, including thermoforming, extrusion, and injection molding[34]. However, the degradation conditions for PBS are relatively harsh, and its degradation time is longer than that of other degradable plastics, such as PLA.

2.4 PCL

PCL is a semi-crystalline polymer with a glass transition temperature of –60°C and a melting point that ranges from 59°C to 64°C. Figure 2c shows the synthesis of PCL by ring-opening polymerization of ε-caprolactone. PCL is highly suitable for controlled drug delivery systems due to its non-toxic properties and high permeability to many drugs. The biodegradability of plastics is closely tied to their composition, and the chemical and physical properties that influence the biodegradation process. Although the degradation rate, which depends on their crystallinity and molecular weight, is relatively slow, they still degrade more rapidly in soil compared to petrochemical plastics[24].

Moreover, the biodegradability of PCL and PBS can be improved through copolymerization with other aliphatic polyesters. Furthermore, blending different polymers can further improve their performance and broaden their range of applications. For instance, blending PLA with PCL - which exhibits high toughness and a low glass transition temperature - can effectively reduce the brittleness of PLA. PLA/PCL blends have emerged as promising materials for various applications, including tissue engineering, bone fixation devices, controlled drug release, and food packaging. However, PLA/polyester blends still exhibit poorer thermal stability and mechanical properties, particularly lower impact strength, compared to commodity plastics such as PP.

2.5 PBAT

PBAT is an aliphatic-aromatic biodegradable polyester composed of terephthalic acid (TPA) and 1,4-butanediol (BDO). The aromatic fraction offers excellent physical properties, while the presence of aliphatic chains can lead to degradation under various conditions, including soil degradation, without the need for temperature control[35]. It is typically synthesized through melt polymerization. PBAT exhibits a combination of the properties of polybutylene terephthalate (PBT) and polybutylene adipate (PBA), resulting in excellent flexibility and performance[36]. Due to its favorable biocompatibility and biodegradability, PBAT is widely used in applications such as agricultural films, disposable products, and environmentally friendly packaging materials. However, compared to traditional plastics, PBAT still requires improvement in terms of mechanical properties, thermal stability, and cost. The production cost of PBAT is approximately three times higher than that of low-density polyethylene (LDPE), which presents a significant challenge for its market adoption.

2.6 PPF

In addition to the several mentioned above, poly (propylene fumarate) (PPF) is also a common polymer among petroleum-based biodegradable polymers. Besides PLA, PPF is another widely used polymer in bone tissue engineering therapeutics. PPF is a linear, aliphatic biodegradable polyester composed of alternating propylene glycol and fumaric acid units[37]. The molecular chain of PPF features unsaturated bonds that dedicate high mechanical properties. The presence of double bonds and ester bonds within the PPF structure provides significant advantages. Firstly, the double bonds can form cross-linked networks with themselves or other reagents. Secondly, the ester bonds facilitate hydrolysis, allowing the polymer to degrade into fumaric acid and propylene glycol, both of which can be absorbed by the body[37]. In addition, PPF exists in a liquid state at room temperature, which makes it easy to process. This characteristic allows for various molding techniques such as casting and injection molding, thereby reducing the complexity and cost of manufacturing. Moreover, its liquid form enables better filling of molds and irregularly shaped defect sites, facilitating the formation of polymer networks. However, this feature also poses challenges related to storage and environmental management. PPF-based copolymers have been synthesized to improve the properties of PPF, such as poly (propylene fumarate-co-caprolactone) (PPF-co-PCL), poly (propylene fumarate-co-ethylene glycol) (PPF-co-EG), and poly (propylene fumarate-co-propylene sebacate) (PPF-co-PS). Although these polymers exhibit good biocompatibility and high hydrophilicity, their weak mechanical strength and poor antibacterial activity limit their applications in tissue engineering. Fortunately, new approaches, such as the incorporation of nanofibers into polymer networks, show promise in improving their performance.

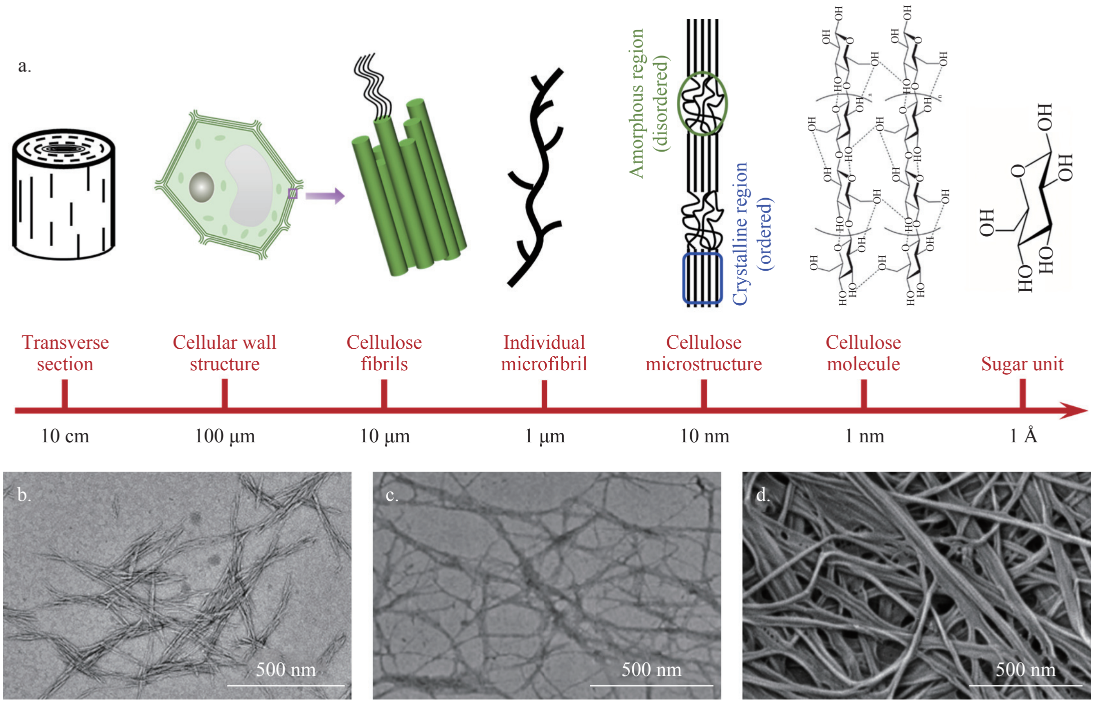
Table 1 presents a comparison of common polymers and their properties and applications in both biobased and petroleum-based degradable polymers.

Table 1 Comparison of common types and properties of biobased and petroleum-based biodegradable polymers

Polymer	Monomer	Origin	Melting point/°C	Strength/ MPa	Density/ $g \cdot cm^{-3}$	Applications	Ref
PLA	Lactic acid	Maize starch, dairy whey, or organic residues	175	21–60	1.21–1.25	Packaging, medical applications	[38,39]
PHB	3-Hydroxybutyric acid	Biomass feedstocks	160–170	40–55	1.25	Agricultural films	[40]
PCL	Chiral hydroxy acids, lactones	Petrochemical materials	55–60	20	1.10	Specialty applications, flexible films	[41,42]
PBS	Succinic acid, 1,4-butanediol		90–120	30	1.23	Packaging, agricultural films	[24]
PBAT	Terephthalic acid and 1,4-butanediol		110–120	11–21	1.23	Compostable packaging, film applications	[39]
PPF	Propylene glycol and fumaric acid		160–175	Variable	1.20–1.30	Biomedical applications	[43,44]

3 Nanocellulose

Nanocellulose can improve the mechanical properties and thermal stability of biodegradable polymers without compromising their biodegradability, unlike the common methods using calcium carbonate and graphene[10]. Cellulose is a polymer composed of glucose units linked by a β-1,4-chain[45]. Figure 3a illustrates the transition from the transverse section of wood to the sugar unit, showcasing a progression from a larger to a smaller scale. Nanocellulose is derived from natural cellulose through physical or chemical degradation, with diameters ranging from 1-100 nm[46,47]. Cellulose comprises dense crystalline regions and amorphous regions with scattered regions in between. The molecular chains in the crystalline region are regular, whereas those in the amorphous region are loose and disordered. Initially, physical or chemical treatment targets the amorphous region before affecting the crystalline region. By controlling mechanical shearing and acid hydrolysis processes, distinct nanocellulose structures can be obtained by deconstructing cellulose in these regions. In general, the nanocellulose family can be classified into three types: cellulose nanocrystal (CNC), cellulose nanofibril (CNF), and bacterial nanocellulose (BNC). CNC and CNF are typically produced through the physical or chemical degradation of natural cellulose into nanoscale cellulose, employing a top-down approach. In contrast, BNC is synthesized by bacteria from low molecular weight sugars, using a bottom-up method[48]. Table 2 compares the basic physicochemical properties of three kinds of nanocellulose.



Note: a. The hierarchical structure of cellulose[10,49]; b, c. transmission electron micrographs of CNC and CNF[50,51]; d. SEM image of BNC[52].

Figure 3 The hierarchical structure of cellulose and the morphological characteristics of different nanocellulose

Table 2 Comparison of CNC, CNF, and BNC

NC	Diameter/ nm	Length/ nm	Shape	Tensile strength/ MPa	Crystallinity/ %	Thermal stability/ °C	Ref
CNC	2-20	100-500	Rod-like	7500-7700	54-88	~220	[53-55]
CNF	1-100	500-2000	Fiber-like	350-500	40-70	~260	
BNC	20-100	Micro to millimeter scale	Sheet- or fiber-like	20-2000	50-60	~300	

3.1 CNC

CNC is mainly prepared by chemical or physical treatment to remove the amorphous region of cellulose and retain the crystalline region of cellulose. Due to the removal of amorphous regions, the proportion of crystalline regions in CNC is increased, resulting in a high crystallinity index, typically ranging from 54% to 88%[53]. CNC is mainly prepared by inorganic acid hydrolysis, the most classic of which is sulfuric acid hydrolysis, which can introduce sulfonic acid groups on the surface of the product. The performance of the obtained CNC varies due to differences in the source of raw materials. Generally, CNCs consist of rod-like segments with lengths ranging from 100 to 500 nm and diameters from 2 to 20 nm, as shown in Figure 3b. Additionally, CNC exhibits a high aspect ratio, exceptional axial stiffness, a Young's modulus, tensile strength (7.5-7.7 GPa), thermal stability (up to 220°C), a low coefficient of thermal expansion, and density[56].

3.2 CNF

CNF is primarily produced by processing cellulose raw materials using intense mechanical shear force. During this treatment, the amorphous region is not entirely removed, resulting in a certain degree of retention. Therefore, the final product consists of both crystalline and amorphous domains. CNF as a novel cellulosic material was first made from softwood pulp after several high-pressure homogenizing mechanical treatments. In this treatment condition, due to the high shear force, a strong interwoven network of nanofibers with crystalline and amorphous states is generated (Figure 3c), and the product has a large ratio of length to diameter, forming a shear-thinning gel with thixotropic properties when suspended in water. Depending on the preparation conditions, cellulose can be disintegrated to flexible CNF with diameters ranging from 1 to 100 nm and lengths typically in the micrometer range. The strength of CNF typically ranges from 350 to 500 MPa, with a crystallinity level of 40% to 70%. Furthermore, their degradation temperature is remarkably high, reaching up to 260°C. Although the mechanical method of CNF preparation produces no corrosion and no pollution, it requires high energy consumption[57]. Therefore, recent research has focused on enhancing fibrillation and reducing energy demand through the combination of various biological and chemical pretreatments, which has become a mainstream trend in the preparation of CNF[12].

3.3 BNC

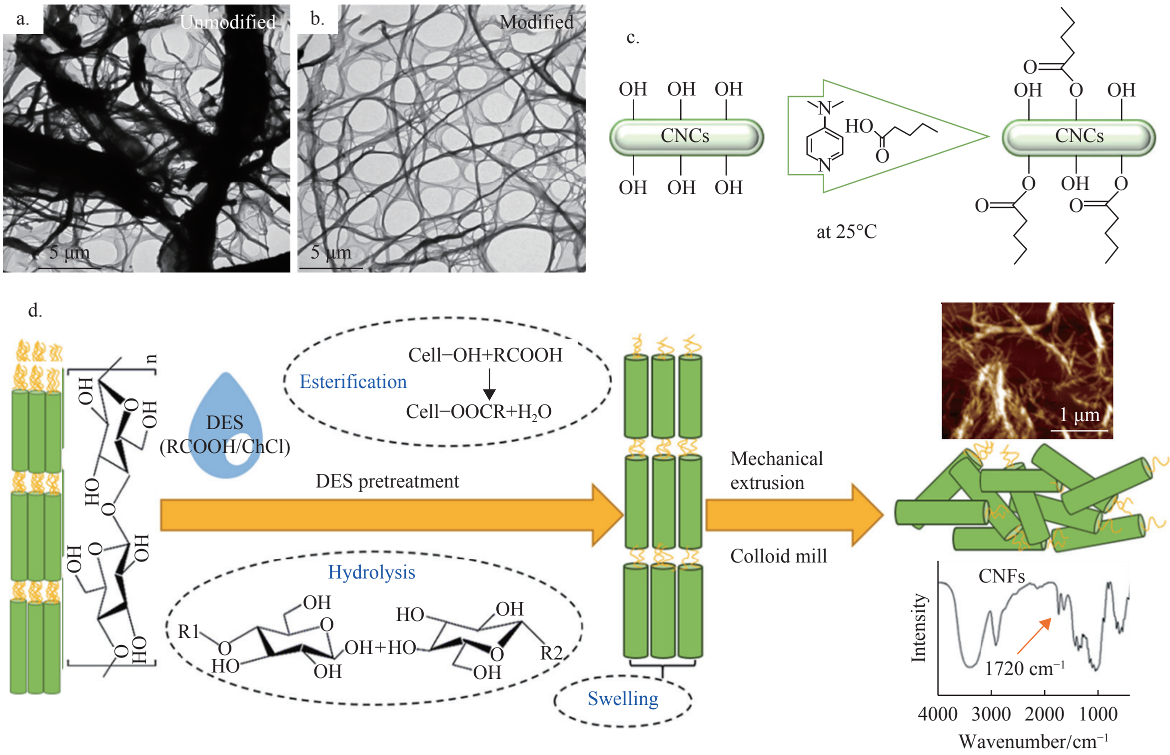
BNC is a high-purity form of cellulose synthesized and secreted by the Gluconoacetobacter xylinus family, commonly referred to as bacterial cellulose (BC)[58]. This method is known as the bottom-up approach. BC has the same chemical composition as plant cellulose. Functional groups such as carboxyl group and carbonyl group can be introduced in the process of preparing nanocellulose from plant cellulose, but BC contains no functional groups except hydroxyl group. Generally, the degree of polymerization (DP) of BC ranges from 3000 to 9000, with high crystallinity, generally around 80%-90%. In addition, BC does not contain other polymers such as lignin, hemicellulose, or pectin. As shown in Figure 3d, BNC presents thin nanocellulose ribbons, typically 20-100 nm in diameter, which generally need to be cultured in an aqueous medium for several days to two weeks. The crystallinity of BNC is typically around 50%-60%, while its strength can range from 20 MPa to 2000 MPa. However, BNC is less commonly used than CNC and CNF in polymer composite reinforcement, possibly due to the lengthy preparation time associated with BNC.

4 Chemical modifications of NC for reinforcing degradable polymers

There have been issues regarding the poor compatibility of nanocellulose with hydrophobic polymers and the uneven dispersion of nanocellulose within these matrices owing to the abundance of hydroxyl groups on the surface of nanocellulose. There are two common ways to address these issues. One approach is to add interface compatibilizers, such as maleic anhydride-grafted polypropylene (MAPP)[59] and polyethylene oxide (PEO)[60]. Another method is the chemical modification of nanocellulose, which is the focus of this study. Its advantages include a wide range of chemical reaction types, high grafting efficiency, mild reaction conditions, and various optional functional groups for subsequent modifications. In fact, in the process of chemical modification, interface compatibilizers are sometimes added to assist. In terms of the types of chemical reactions, this study will discuss several commonly used strategies for the chemical modification of nanocellulose in the reinforcement of degradable polymers. These strategies include esterification, oxidation, silylation, and polymer grafting, which have been the focus of recent advancements.

4.1 Esterification

Esterification, which can be carried out in either homogeneous or heterogeneous form, is one of the most commonly utilized chemical methods. For many years, the acetylation achieved through the combination of acetic anhydride and acetic acid has been a central focus of both research and industry. Due to its remarkable hydrophobic properties and thermal stability, acetylated nanocellulose is increasingly utilized as a reinforcement material based on non-polar polymeric matrices, including various biodegradable polymers. In order to improve the compatibility of CNF and PLA, Ren et al. used acetic anhydride and DMAP in NMP to esterify CNF[61]. The morphology and dispersion state of CNF in the PLA matrix are shown in Figure 4a and 4b. The untreated CNF presented relatively thick bundles, while the esterified CNF exhibited a long fiber network structure. Various tests have shown that the crystallization properties and melt elasticity of PLA/CNF composites were significantly improved compared with neat PLA, as a three-dimensional network-like structure was formed in the composite. The introduction of 2 wt% acetylated CNF significantly improved the foaming behavior of PLA, and the high expansion-ratio fully-biobased PLA foam was successfully prepared by using CO_2 as foaming agent. This research holds promise for the development of low-density, biodegradable PLA foams for thermal insulation and green packaging applications. Jamaluddin et al. conducted a similar study, in which they prepared acetylated CNF (ACNF) and composites[62]. Without reducing thermal stability, the hydrophobicity of ACNF/PLA film increased due to the increase in surface roughness. The addition of 1 wt% ACNF increased the tensile strength of the film by 25%, reaching 37.6 MPa, while the tensile strength of pure PLA was 30.1 MPa. Hu et al. produced biodegradable foamed nanomaterials by melt-blending 5 wt% acetylated cellulose nanocrystals (ACNC) with PBS[63]. Surface acetylation of ACNC converted hydrophilic hydroxyl groups into hydrophobic acetyl groups, enhancing compatibility between ACNC and PBS through similar ester groups. Furthermore, ACNC served as nucleation agents, promoting the heterogeneous nucleation of bubbles and the formation of cell nucleation sites during the foaming process.



Note: a. and b. TEM images of the PLA/CNF composites with unmodified and modified CNF[61]; c. reaction schematic of esterification[64]; d. schematic diagram for preparation of CNF through DES pretreatment[65].

Figure 4 Effect comparison, mechanism, and route of esterification modification

In cellulose esterification, the degree of substitution (DS) is a crucial parameter that reflects the degree to which hydroxyl groups in cellulose molecules are replaced by ester groups. Specifically, DS represents the number of hydroxyl groups replaced in each glucose unit. In cellulose molecules, each glucose unit in cellulose generally possesses three replaceable hydroxyl groups (at the C2, C3, and C6 positions), leading to a theoretical maximum DS value of 3[21]. Nanocellulose with a high DS has better compatibility with matrix due to the improvement of hydrophobicity. Mugwagwa et al. prepared acetylated hemicellulose (AH) and acetylated CNC (ACNC) using acetic anhydride and sulphuric acid as the catalyst[66]. The DS significantly affected the dispersion of ACNC in AH and PCL. Firstly, at lower DS values, ACNC particles became entangled and agglomerated within AH. Secondly, as the DS of ACNC increased, the thickness of the AH-CNC/PCL film decreased, indicating that ACNC can achieve uniform dispersion within the matrix, resulting in improved compatibility and adhesion.

In addition to the commonly used acetic anhydride, many esterification modification methods have been developed. Celebi et al. used n-octadecyl isocyanate to chemically modify nanocellulose (ISO-NC), which was prepared from MCC by classical sulfuric acid hydrolysis[67]. Isocyanate modification with n-octadecyl isocyanate improved the distribution of nanocellulose in the PCL matrix, enhancing interface compatibility between PCL and ISO-NC and improving the dynamic mechanical and rheological properties of the composite. Shojaeiarani et al. introduced a time-efficient esterification method using valeric acid (4-Dimethylaminopyridine) to improve compatibility between CNC and PLA (PLA-e-CNC)[64]. The reaction schematic of the esterification process is illustrated in Figure 4c. As an emerging green solvent, deep eutectic solvents (DESs) demonstrate excellent solubility and reactivity, effectively dissolving and removing impurities such as lignin and hemicellulose, thereby enhancing the reactivity of CNF and facilitating the esterification reaction. Liu et al. demonstrated the successful use of different carboxylic acid-based DESs as pretreatment media for the production of CNF[65]. As shown in Figure 4d, the DESs facilitate esterification modification and effective swelling of cellulose. Furthermore, the introduction of carboxylic groups during the esterification process improved the dispersibility of CNF within the PLA matrix, resulting in improved mechanical strength of the CNF/PLA composites.

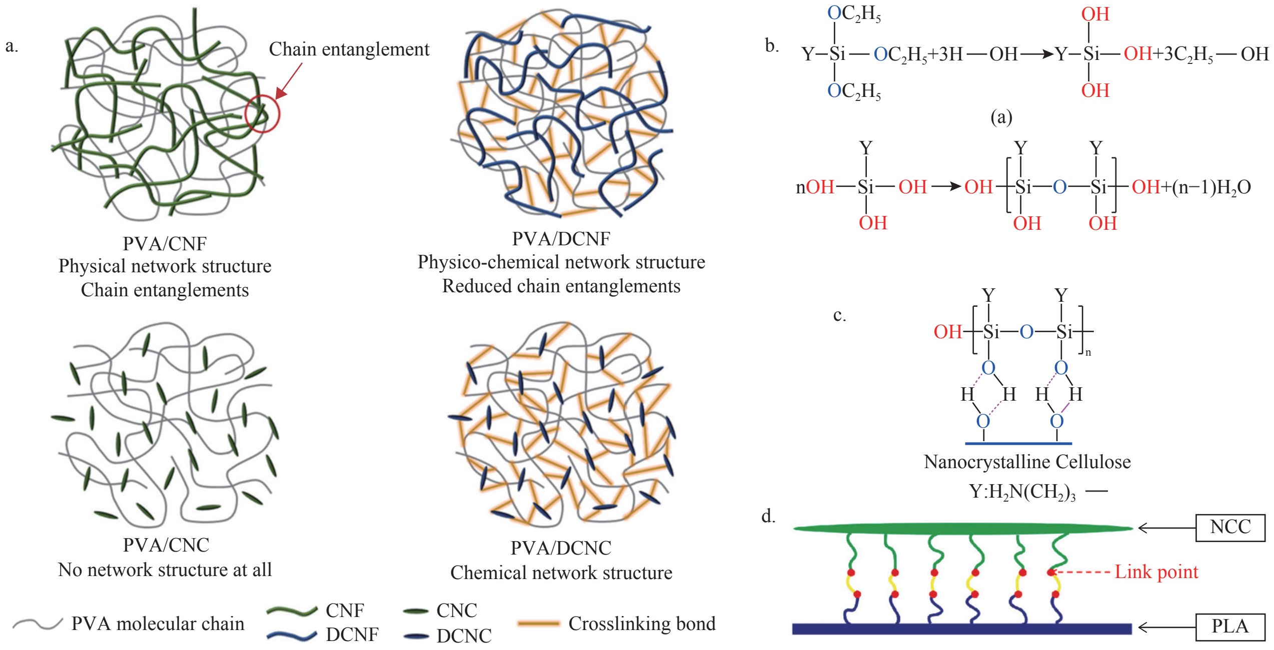
4.2 Oxidation

In addition to esterification, oxidation reactions can also be used to introduce carboxylic acid or aldehyde functional groups onto the surface of cellulose. Wherein, the most widely used method for oxidizing cellulose is the TEMPO-mediated oxidation, which is commonly used in the presence of sodium hypochlorite (NaClO) and sodium bromide (NaBr) for the selective conversion of the C6 hydroxyl group of nanocellulose to carboxylate groups. These carboxylate groups can serve as scaffolds for the assembly of metal ions or alkylammonium ions through ion exchange, enabling the production of nanocellulose with varying functionalities. However, this process can also result in the formation of certain aldehyde groups. In order to avoid the formation of aldehydes and achieve optimal selectivity for the primary hydroxyl group, the reaction should be carried out in an alkaline environment with a pH ranging from 9 to 11.

Fijoł et al. utilized a four-step method to prepare PLA matrix composites reinforced with uniformly dispersed TEMPO-oxidized CNF (TCNF)[68]. The integration of TCNF into the PLA matrix led to significant improvements in the mechanical properties and toughness of the filters, highlighting the reinforcing impact of the uniformly dispersed nanofibers. The Pickering stabilization process is an efficient and highly versatile method for preparing cellulose-based nanocomposites. This technique involves the stabilization of interfaces between two immiscible liquids using solid particles[19]. Li et al. improved the dispersion of TEMPO-oxidized bacterial cellulose (TOBC) in PLA matrix using the Pickering emulsion method, which contributed to the formation of three-dimensional networks and cross-linked structures, facilitating the crystallization of PLA as a nucleating agent[69]. The PLA/TOBC filament was then fabricated via screw extrusion, with the optimal TOBC content determined to be 1.5 wt%.

In addition to its widespread use in composites with PLA, TEMPO-oxidized nanocellulose can also be employed to reinforce other biodegradable matrices. It is well known that due to the water solubility of PVA, PVA-based plastics exhibit low mechanical strength in water environments. Luo et al. introduced inorganic calcium phosphate oligomers (CPO) in TEMPO oxidized CNF (TOCN) reinforced PVA[70]. The CPO oligomer was able to cross-link PVA chains with TOCN under the action of stretching and water evaporation. Therefore, PVA/TOCN/CPO films exhibited hydrophobicity and good wet strength. In addition, PVA/TOCN/CPO films had excellent self-healing efficiency due to the dynamic regeneration of hydrogen bonds and coordination interactions within the PVA matrix. Espinosa et al. prepared TEMPO-mediated oxidation lignin-containing nanocellulose from wheat straws to reinforce PVA films using solvent casting[71]. Although nanocellulose is hydrophilic, it reduces the hydrophilicity of the PVA matrix, which reduces the absorption of water vapor. Furthermore, the inclusion of nanocellulose promotes increased entanglement within the film matrix, resulting in higher gas molecule density and a more convoluted diffusion pathway. Poly (propylene carbonate) (PPC) is also an important biodegradable polymer, synthesized from propylene oxide and carbon dioxide. Jiang et al. achieved significant reinforcements in the impact strength and tensile strength of PPC/PHB composites, increasing them by 2.6 and 1.35 times, respectively, through the use of TEMPO-oxidized CNC.[72] These improvements were attributed to the ample area of the hydroxyl groups on the CNC, which facilitates hydrogen bonding with the carbonyl and hydroxyl groups of the PPC and PHB molecular chains. This interaction results in stronger interfacial adhesion, requiring more energy to break. Additionally, the incorporation of 0.7 wt% CNC led to an impressive 88.9% reduction in the overall oxygen permeability coefficient, and the authors provided a comprehensive analysis of the mechanisms involved.

In addition, periodate oxidizes the C2 and C3 hydroxyl groups of glucose units to form aldehyde groups and cleaves the C2-C3 bond, resulting in the formation of 2,3-dialdehyde cellulose. Lee et al. introduced the dialdehyde groups by periodate oxidation of CNF and CNC (DCNF and DCNC), which could act as a crosslinking agent[73]. The dialdehyde nanocellulose-reinforced PVA nanocomposite film was prepared to improve the water resistance of PVA. In terms of thermal stability, both PVA/DCNF and PVA/DCNC exhibited a decomposition temperature that exceeded that of neat PVA by more than 100°C. This represents a significant enhancement in thermal stability compared to previously reported research. Figure 5a shows the physicochemical structure changes of PVA nanocomposite films. PVA/DCNF has a chemical network structure due to cross-linking reaction with the physical network structure of CNF, while PVA/DCNC only has a cross-linked chemical network structure. Hydrophobicity test showed that while physical network structures are important, chemically formed network structures are more significant in enhancing the water resistance.



Note: a. Physicochemical structure of PVA-based composite film[73]; b-d. alkylation mechanism of SCNC[74]

Figure 5 Reinforcement comparison of CNF and CNC and alkylation mechanism

4.3 Silylation

Silanes, such as 3-aminopropyltriethoxysilane (APS), 3amino-propyl triethoxysilane (KH-550) and *γ*-aminopropyltriethoxysilane (APTES), are commonly used as commercial coupling agents, feature an alkoxysilane group that can establish covalent bonds with hydroxyl rich surfaces on one end and diverse functional groups on the other end that can be customized to suit specific matrix requirements[75]. The silane coupling agent is hydrolyzed to form silanol groups, which readily react with the hydroxyl groups on the surface of the nanocellulose to form Si-O-C chemical bonds[76]. Silylation has become another promising and commonly used surface modification method, introducing silyl groups on the surface of nanocellulose to improve the compatibility with non-polar matrices. Compared with other nanocellulose modification methods, silylation offers significant advantages due to its simplicity of reaction and purification. In general, this reaction only requires stirring for 5-20 h at room temperature, with a pH of 3-5. Jin et al. successfully prepared a silicated CNC (SCNC) by hydrolyzing MCC with sulfuric acid and dispersing KH-550 in ethanol, adjusting pH to 3 with acetic acid and reacting at 27°C for 2.5 h[74]. Alkylation mechanism of SNCC is shown in the Figure (5b-5d). Initially, in an acidic condition, the -O-C_2H_5 groups of KH-550 were hydrolyzed to generate -Si-OH (Figure 5b). Subsequently, the -Si-OH in KH-550 is anticipated to undergo dehydration and condensation processes, leading to the formation of oligomers (Figure 5c). These oligomers, rich in hydroxyl groups, can subsequently establish hydrogen bonds with the hydroxyl groups present on the surface of CNC or form ether bonds by dehydration and condensation. Silanization modification significantly improved the interfacial compatibility between PLA and SNCC. Optimal SCNC addition enhanced the air permeability, UV-visible reflectivity, mechanical properties, and thermal stability of composite films. Notably, the PLA/SNCC composite films containing 0.5 wt% SCNC exhibited a 53.87% increase in tensile strength and an 87.9% decrease in air permeability compared to pure PLA films.

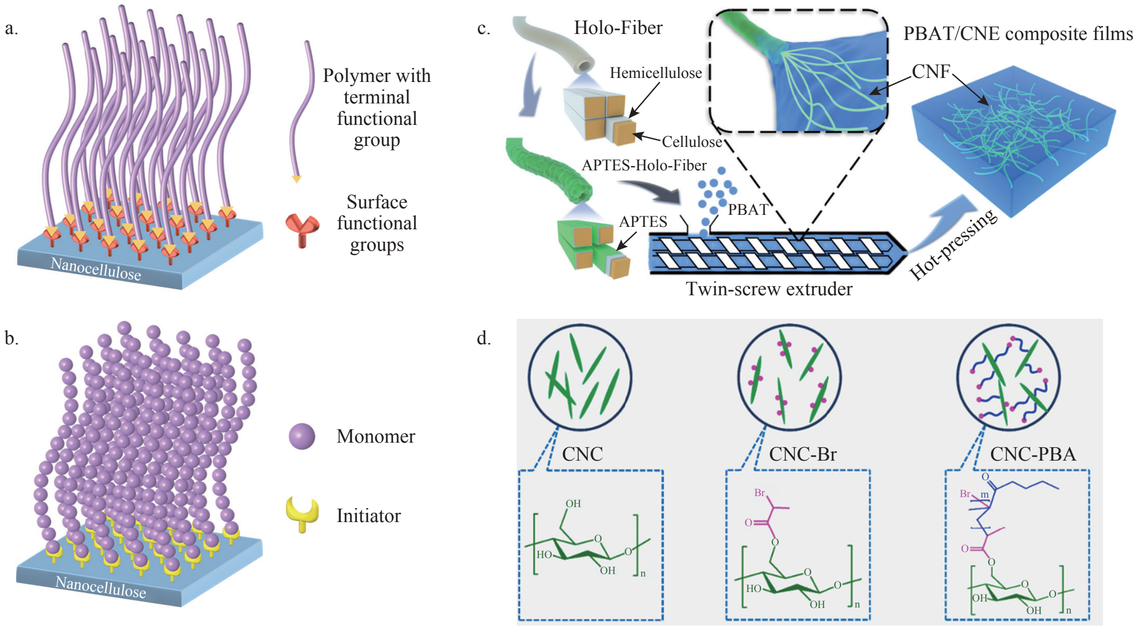
Indeed, silylation is less effective than other modification methods like acetylation in producing hydrophobic nanocellulose with high DS. Excessive silylation levels would cause crystal disintegration, resulting in the loss of original morphology of cellulose. Achieving an optimal balance between the silylation level and cellulose morphology often requires experimenting with various reaction conditions, including different silane reagents, pH, temperature, and reaction time[21]. Dhali et al. dispersed CNC in ethanol solution, used acetic acid to adjust pH to about 4.0, and used 5% triethoxyvinylsilane (TEVS) or trimethoxyphenylsilane (TMPS) to modify CNC silylation at 48°C for 2.5 h with stirring, in order to prepare CNC-VS and CNC-PhS[77]. In order to improve the effective grafting rate of the silanol groups, the suspension was cured at 110°C. CNC-VS and CNC-PhS were melt blended into the PBAT matrix and hot-pressed into composite films. The modified CNC was uniformly dispersed in the PBAT matrix as an additive. In comparison to the pristine PBAT films, the tensile strength of the composite film was increased by 12%, the modulus was increased by 58%, and the permeability to water vapor and oxygen was greatly reduced.

Numerous studies indicate that the effects of silylation vary among different types of nanocellulose. Goussé et al. observed that the silylation process had a less deleterious impact on the crystal morphology of CNF compared to CNC.[78,79] In addition, the silylated BNC still needs to be further studied and improved in reinforcing polymers. Sai et al. conducted a trimethylsilylation (TMCS) reaction on BNC to produce hydrophobic bacterial cellulose aerogels[80]. Despite this, a very low DS in the silylated BNC (≤0.132) was observed, which was comparable to the unmodified BNC.

4.4 Polymer grafting method

The hydroxyl functional groups present on nanocellulose serve as chemical attachment points or “handles”, enabling them to react and bond with various chemicals. This unique property allows for the grafting of small organic molecules onto nanocellulose through chemical reactions, as well as the growth of macromolecular polymers from its structure. Surface grafting is recognized as an effective and versatile method for achieving highly stable suspensions in non-polar solvents and is widely used in the field of nanocellulose-reinforced polymers. Polymer grafting can be categorized into two approaches: “grafting onto” and “grafting from”.

As illustrated in Figure 6a, “grafting onto” involves attaching the polymer to nanocellulose, whereas in the “grafting from” approach, the monomers are directly grown from nanocellulose surface[21]. The “graft onto” method relies on attaching a coupler (linker) and a polymer with a reactive end group to the nanocellulose surface via covalent bonding. This method is popular for its simplicity and its ability to control molecular weight due to the steric hindrance caused by polymer chains, although the number of graft functional groups achieved through this approach is limited. In contrast, the “grafting from” method involves first introducing an initiator onto the nanocellulose and then growing the monomer directly from its surface, which was first posed by Stensted et al.[81] This method can generate polymer grafting with a higher density compared to the graft-onto method. Nevertheless, characterizing the properties of the resulting polymers poses a challenge. The complexity of this approach may be attributed to initiating a polymerization reaction directly on the surface of nanocellulose, leading to a diverse range of polymers with different structures and properties. Overall, both methods have their advantages and disadvantages, and the appropriate choice of grafting technique should be based on the specific needs and application contexts.



Note: a-b. Schematic illustration of “grafting onto” and “grafting from”[21]; c. preparation process for PBAT/CNF films[82]; d. ARGET ATRP of BA from CNCs surface[83].

Figure 6 Mechanism and route of grafting modification

The graft modification of nanocellulose has been extensively studied and applied to reinforce a variety of biodegradable polymers. To address the compatibility and dispersion challenges of nanocellulose in the PBAT matrix, both in-situ polymerization and surface modification techniques were explored. However, the high temperature of 240°C during the reaction poses a potential risk of degradation. Although some esterified nanocellulose improved the tensile strength and modulus of PBAT, the elongation at break of the composite significantly decreased[84]. As shown in Figure 6b, Wang et al. selected a hemicellulose-rich holocellulose fiber for silanization and in-situ polymerization to prepare CNF, and then prepared PBAT/CNF composite films by twin-screw extrusion combined with hot pressing[82]. The role of hemicellulose in hemicellulose-rich holocellulose fibers is to promote cell wall swelling. Compared with the neat PBAT, the addition of 1 wt% CNF fillers resulted in an 82% increase in tensile modulus, with the PBAT/CNF films exhibiting a tensile strength of 26 MPa and an elongation of 372%. Niu et al. prepared the aliphatic chains-grafted CNC (ECNC) with different aliphatic chain lengths (C5-C18) using valeryl chloride, octanoyl chloride, dodecanoyl chloride and stearoyl chloride to obtain EVCNC, EOCNC, EDCNC, and ESCNC, respectively[85]. All four of these different acyl chlorides can serve as heterogeneous nucleating agents, contributing to the core-corona structure of the ECNC. This corona structure containing aliphatic chains is crucial to improve the toughness of PLA, which ensures the high efficiency flexibility and mobility of PLA molecular chain. Compared with other ECNC, the surface of ESCNC contains a large number of longer fatty chains (C18), which greatly increases the specific surface area of ESCNC and can interpenetrate with PLA molecular chains to form more nucleation sites. The authors proposed a mechanism for synergistic toughening based on the aliphatic chains and core-shell structure. Specifically, one mechanism involves physical entanglement and surface bonding of intermolecular forces, while the other is through soft hydrophobic shell to reduce stress. Chuensangjun et al. used sugarcane bagasse bleached pulp (BBP) as a raw material to prepare TEMPO-oxidized CNF, and then synthesized a grafted nanocomposite, BBP-TOCN-g-PLA, through a dual-temperature process[86]. This approach significantly enhanced surface grafting efficiency, resulting in composites with high crystallinity (>76%) and a small crystallite size of 3.8 nm. To overcome the aggregation of CNC in PBS and improve the nucleation and reinforcing of CNC, Kwak et al. modified the surface of CNC with PBS oligomers (BS-CNC) through a two-step esterification process[87]. The PBS/BS-

CNC straw demonstrated satisfactory mechanical strength under both dry and wet conditions, exhibiting a well-balanced performance compared to commercial products.

Two of the most commonly used pathways for grafting-from include surface-initiated atom transfer radical polymerization (SI-ATRP) and ring opening polymerization (ROP). Yin et al. explored the surface grafting of CNC with PBA through electron transfer (ARGET) atom transfer radical polymerization (ATRP), enhancing their thermal stability and compatibility with PLA (Figure 6c)[83]. The treated PLA nanocomposites showed significant improvements in mechanical properties and thermal characteristics, particularly at a CNC-PBA400 content of 2 wt%, where tensile strength, elongation, and Young's modulus increased by approximately 350%, 100%, and 120%, respectively. ROP facilitates high-density grafting while preserving the structural integrity of nanocellulose, and it stands as a pivotal approach to addressing the dispersion and compatibility challenges associated with nanocellulose-reinforced polyester composites. Carlsson et al. have shown that extended reaction times do not invariably result in a higher density of PCL grafted chains on the CNC surface[88]. Lalanne-Tisné et al. studied the ROP polymerization of CNF under mild conditions using rac-Lactide and N, N-dimethyl aminopyridine (DMAP) as organic catalysts[89]. The authors discovered that the grafting ratio could be tuned by modifying the experimental parameters, achieving as high as 74%. Lönnberg and colleagues successfully grafted PCL of diverse lengths onto CNF using ROP technique (PCL-g-CNF)[90]. This method permitted adjustments to both the grafting density and the length of the PCL chains. Cellulose grafted with the longest PCL chains had the best mechanical properties reinforcement effect.

Table 3 provides an overview of the nanocellulose modification approaches employed to improve the degradable polymers along with a comparison of processing techniques and the main properties of composites.

Table 3 Summary of the mechanical properties obtained from some representative studies on surface modification nanocellulose-reinforced biodegradable polymers

Raw material/ Nanocellulose	Polymer matrix	Progressing technique	Proportion of NC/wt%	Surface modification method	Main performance	Ref.
MCC/CNF	PLA	Solution casting	1.00	Acetylation	TS: 37.6 MPa; EB: 3.1 % Contact angles were increased from 70.2° (PLA) to 85.9°.	[62]
Cotton linter/CNC	PBS	Melt-compounded and hot pressing	1.00-10.00	Acetylation	Flexural strength and modulus were increased by 50.0% and 34.1% compared to the unmodified composite when the addition of ACNC was 5%.	[63]
Wheat straw/CNC	PCL	Solution casting	10.00-50.00	Acetylation	WCA was increased from 24.59° (PCL) to 82.48°.	[66]
MCC/CNC	PCL	Solution casting	5.00-10.00	Esterification with N-octadecyl isocyanate	T_{max}: 415°C (higher than neat PCL)	[67]
Hardwood bleached kraft pulp/CNF	PLA	Solution casting/injection	5.00-15.00	Esterification with DES	TS: ~60 MPa	[65]
CMF	PBS	Solution casting	10.00-50.00	Esterification	TS: ~36 MPa	[91]
MCC/CNC	PBS	Melt blending and hot pressing	0-7.00	Esterification with succinic anhydride	TS: ~39 MPa; YM: ~350 MPa; EB: ~160%	[92]
CNF	PLA	Melt-extrusion	5.00	TEMPO-mediated oxidation	TS: ~33 MPa The adsorption capacity towards copper ions (234mg·g_{NF}^{-1}) and separation efficiency for removal of microplastics (54%) were increased.	[68]
CNF	PVA	Solution casting	5.00-20.00	TEMPO-mediated oxidation	TS: 176 MPa; EB: 23% TS was 16.1 MPa in water for 7 days (similar to PE in the dry state).	[70]
Wheat straw/CNF	PVA	Solution casting	1.00-7.00	TEMPO-mediated oxidation	TS: 58.86-72.76 MPa; YM: 4.29-5.05 GPa; EB: 200%-1000% The antioxidant capacity of the films was increased and ability to block UV-light increased from 10% for PVA to >50%.	[71]
MCC/CNC	PPC and PBS	Solution casting	0.30-1.00	TEMPO-mediated oxidation	TS: 22.1 MPa; IS: 2.4 kJ·m^{-2} The overall oxygen permeability coefficient was reduced by 88.9% with the incorporation of 0.7 wt% CNC.	[72]
MCC/CNC	PLA	Solution casting	0.50-2.00	Silylation with KH-550	TS: 12-43 MPa; EB:3%-8% Air permeability decreased by 87.9% with the incorporation of 0.5 wt% SCNC.	[74]
CNC	PBAT	Melt blending and hot pressing	3.00-5.00	Silylation	TS: 30.5 MPa; YM: 66.6 MPa; EB: 698% WCA and T_c increased to 79.1° and 103.06°C.	[77]
Bleached softwood kraft fibers/CNF	PBAT	Melt-compounded and hot pressing	0.50-5.00	Silylation	TS: 26 MPa; YM: 117 MPa; EB: 372%	[82]
MCC/CNC	PLA	Solution casting	1.00	Esterification grafting	TS: 30-50 MPa; EB: 68%-108%	[85]
Cotton/CNC	PLA	Solution casting/ hot pressing	1.00-5.00	Grafting onto (ATRP)	TS: 77.43-125.69 MPa; YM: 2.73 GPa; EB: 2.31%-3.17% The initial WCA and T_0 of CNC increased from 50° to 120° and from 150°C to 270 °C, respectively.	[83]
MCC/CNC	PLA	Solution casting	1.00-5.00	TEMPO-mediated oxidation and PEG grafting-onto	TS: 30.9-47.54 MPa; YM: 2.10-4.30 GPa; EB: 1.27%-2.12% T_0: 330.65°C; T_{max}: 367.10°C.	[93]
CNC	PLLA	Solution casting	5.00	Periodate oxidation and glutamic acid grafting	TS: 39 MPa; YM: 2.82 GPa; EB: 3.8%	[94]
CNF	PLA	Melt-extrusion/hot pressing	1.00	Isocyanate grafting-onto	TS: 63.3-75.1 MPa; YM: 1.3-1.5 GPa; EB: 6.1%-7.2% T_0: 355.8°C-360.7°C; T_{max}: 383.83°C-389.6°C.	[95]
CNC	PBAT	Solution casting	0-0.03	In-situ grafting	TS: 31 MPa; YM: 68 GPa; EB: 928% T_c: 65.8°C;	[96]

Note: Compressive strength (CS); Tensile strength (TS); Young's modulus (YM) and elongation at break (EB); Impact strength (IS); Peak degradation temperature (T_{max}); Initial degradation temperature (T_0); Crystallization temperature (T_c); Water contact angle (WCA).

5 Biodegradability

5.1 Biodegradation mechanism and effect factors

Compared to traditional petroleum-based plastics, biodegradable polymers degrade due to a combination of their specific chemical structure, microbial action, and excellent environmental adaptability. These properties make biodegradable polymers an environmentally friendly and efficient alternative, contributing to reduce the environmental stress caused by traditional plastics. The degradation mechanism of biodegradable polymers involves a synergistic effect of both abiotic and biotic factors[97]. Specifically, the macromolecular structure of the polymer is exposed to outdoor conditions, which leads to its weakening through mechanical, chemical, light, thermal, and other transformations. This process initiates biotic involvement, which encompasses three main processes: physical biodegradation, chemical biodegradation, and the interaction between microorganisms and polymers to form new macromolecules[4].

There are many factors affecting the degradation of polymers, in addition to their own inherent characteristics (such as chemical structure and molecular weight), including humidity, temperature, pH, and other environmental conditions[98]. Various methods can be used to evaluate the degradability of polymers, including cycle tests, biodegradation experiments, determination of degradation rates, and characterization of degradation products.

5.2 Biodegradability of nanocellulose/biodegradable polymer composites

Nanocellulose stands out as a promising filler for biodegradable polymers, offering significant advantages in reinforcing mechanical properties and thermal stability while preserving biodegradability of composites. It has been reported that in addition to increasing the strength of composites, nanocellulose is expected to promote the degradation process of composite materials, because nanocellulose has a large specific surface area[99]. The cellulose/PLA film prepared by Xu et al. completely degraded after being buried in soil for 45 days, whereas the degradation percentage of the neat PLA film only reached 68% after 90 days in soil[100]. Morelli et al. reinforced PBAT with grafted CNC, resulting in an improved elastic modulus and reduced water vapor permeability. Notably, the addition of 5% chemically modified CNC did not adversely affect the biodegradability of PBAT, as demonstrated in a bio-fragmentation evaluation conducted over a period of 30 to 180 days[101]. Mai et al. conducted a life cycle assessment (LCA) that found the environmental impact of the isocyanate-modified CNF/PLA composites to be lower than that of maize grain-based PLA, showcasing the sustainability of composites[95].

However, the practical application of nanocellulose is influenced by a variety of factors, including processing techniques, the choice of matrix material, and the modification strategies. While these strategies improve the compatibility of nanocellulose with the polymer matrix, they may also potentially affect the biodegradability of the final product. Although modifiers and compatibilizers can greatly improve the mechanical strength and toughness of composites, further research is necessary to investigate their interactions with the matrices and their behavior during the biodegradation process. Therefore, to ensure that nanocellulose-reinforced biodegradable composites retain their exceptional biodegradability in environmental conditions, it is crucial to systematically investigate various modification strategies and their impacts on biodegradability.

6 Application

After chemical modifications, the dispersion of nanocellulose in the biodegradable plastic matrix is enhanced, improving the compatibility and interfacial binding force between the two components. The excellent reinforcing properties, biocompatibility, degradable nature, and barrier properties of modified nanocellulose-reinforced degradable polymer composites make them widely used in packaging, biomedical engineering, automotive and aviation industries, as well as barrier films and other fields.

6.1 3D Printing

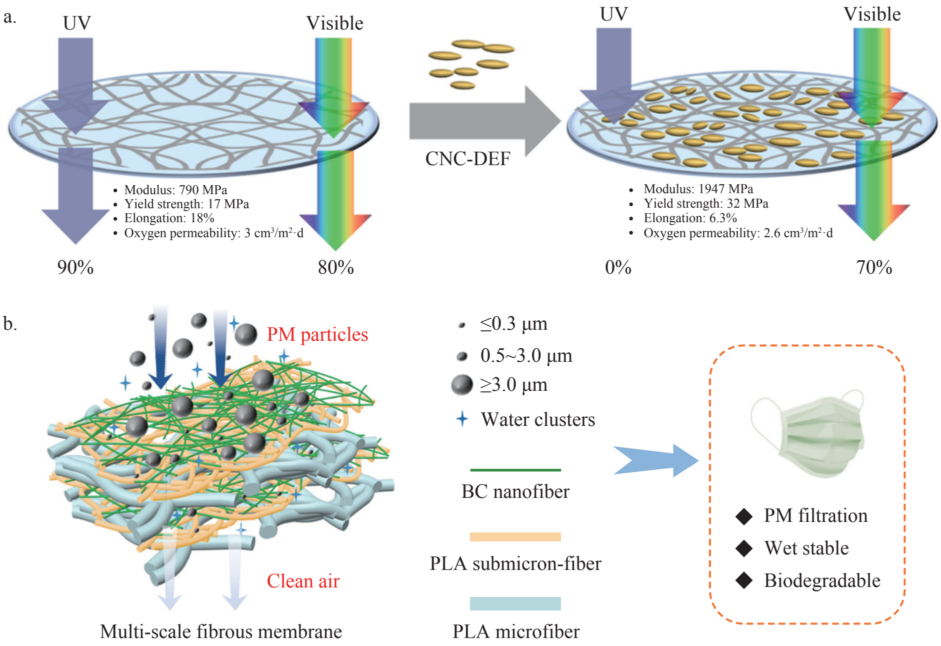
3D printing technology allows for precise control over the shape and structure of materials, which is essential for creating objects with complex shapes or specific geometries. Chemically modified nanocellulose can reinforce the mechanical properties of biodegradable polymers, resulting in composite materials that are more stable, stronger, and capable of withstanding greater physical stresses, making them ideal for printing intricate structures. Moreover, the alterations in molecular structure brought about by chemical modification may improve the machinability of the materials, ultimately enhancing the accuracy and efficiency of the 3D printing process. Li et al. prepared PLA/TEMPO-oxidized BC nanocomposites in the form of filaments using the Pickering emulsion method and subsequently printed them using a 3D printer[69]. They confirmed the suitability of the composites for 3D printing by evaluating the flow properties of the samples. The printed spline surfaces were smooth and free of defects. 3D printing can also serve as a method for preparing composites. Chen et al. used the prepared PLA/PCL/TOBC ternary composites for 3D printing, which provides an opportunity to produce fully biodegradable 3D printed parts for a wide range of applications such as biomedicine and food packaging[102].

6.2 Packaging

As environmental awareness continues to grow, the demand for degradable packaging materials is steadily increasing. Chemically modified nanocellulose reinforces the mechanical properties and thermal stability of polymers, thereby increasing their reliability during both production and use. Mendoza et al. modified a novel UV-absorbent phenol diester on CNC (CNC-DEF) using a click-based copper catalyzed reaction[103]. The CNC-DEF exhibited excellent dispersion in the PVA matrix, resulting in transparent films with complete UV protection and high transparency. The addition of CNC-DEF also improved the mechanical strength, modulus, and oxygen barrier properties of the composite film, making it a promising material for industrial and packaging applications. CNCs grafted with DEF exhibited outstanding UV-blocking and reinforcement properties as nanofillers in PVA films, as demonstrated in Figure 7a. Montero et al. prepared modified-CNF/PBAT composite films with outstanding thermal stability for application in the food industry[104]. In order to validate this concept, the authors employed the composite film in strawberry packaging and observed that after 15 days of preservation, the film with 0.5 wt% modified CNF demonstrated improved preservation properties, reduced weight loss, and absence of fungal contamination. These results suggest that the modified-CNF/PBAT composite films exhibited antibacterial effects against Salmonella and Listeria monocytogenes, potentially serving as a viable alternative to conventional materials in food packaging.

6.3 Filter devices

Wastewater treatment is currently a significant challenge, and



Note: a. Schematic representation of the UV-blocking and reinforcing effect of CNC-DEF in PVA[103]; b. schematic representation of the PM filtration process[105].

Figure 7 UV-blocking and filtration properties of nanocellulose/biodegradable polymer composite membranes

the development of sustainable and efficient adsorption materials is an effective solution[106]. Yi et al. successfully prepared hydrophobic CNF/PVA composite aerogel spheres (HCV-ASs) through freeze-drying and subsequent silanization[107]. HCV-ASs demonstrated excellent adsorption properties for weakly polar organic solvents like petroleum ether, ethyl acetate, and toluene, highlighting its potential in wastewater treatment. This research offers a new approach and concept for addressing wastewater treatment issues. Fijoł and colleagues used PLA as the base material and reinforced the composite with evenly dispersed TEMPO-oxidized CNF using three-dimensional (3D) printing technology and fused deposition modeling (FDM) to manufacture fully biodegradable water purification filters[68]. Compared to pure PLA filters, the biobased composite filters showed higher performance while maintaining high permeability. By combining environmentally friendly materials with time- and cost-effective FDM technology, the development of customized water treatment systems has significant application potential in water-scarce areas.

Airborne pollution, including tiny particulate matter (PM) and the pandemic virus, has greatly increased the demand for personal protective materials. However, the mass discarding of disposable non-degradable face masks has caused serious environmental problems. Although there have been reports of bio-based filters, developing biodegradable respirators that are efficient, wet-stable, and have low pressure drop remains a challenge. In order to address this issue, Yang et al. designed a degradable multi-scale fiber filter composed of PLA micro/nanofibers and BC nanofibers[105]. This filter self-assembles a 2D BC nanofiber network using electrospinning technology, and prepares a medium-porosity PLA submicron fiber network through electrospinning technology. This multi-layer micro/nano fiber structure endows the membrane with a low pore size of 1.27 μm and an extended particle flow path, thus enhancing the PM0.3 interception efficiency and durability (Figure 7b). The results demonstrate that the filter has a low pressure drop (104 Pa) with a PM0.3 filtration efficiency exceeding 99.89% and maintains over 99.68% PM0.3 removal efficiency during long-term filtration at 90% relative humidity (RH). This work provides meaningful guidance for the development of biodegradable and efficient protective air filters.

7 Conclusions

This review summarizes the chemical modification strategies in the past five years to improve the compatibility between biodegradable polymers and nanocellulose fillers. The high reactivity of hydroxyl groups on cellulose surface provides a good foundation for modification. Methods such as esterification, oxidation, silylation, and graft modification have successfully introduced hydrophobic groups onto the cellulose molecular chains. This not only enhances the compatibility and interface bonding between nanocellulose and hydrophobic matrices, but also improves the dispersion of nanocellulose in the matrix, which is critical to improving the performance of nanocellulose-based composites. Researchers are increasingly investigating the application of chemically modified nanocellulose-reinforced biodegradable polymers in fields such as 3D printing, food packaging, and filtration. However, there remains a lack of adequate research and discussion regarding the evaluation methods and case studies assessing the actual degradability of these composites.

8 Prospects

Despite numerous studies on the chemical modification of nanocellulose, only a few have achieved the desired improvement effect. In particular, research on nanocellulose to reinforce different biodegradable polymers exhibits notable variations, with a preference for specific modifications methods. Within the context of this study, the investigation of nanocellulose composites with PLA is particularly active, covering four methods. However, in the case of other polymers like PBS, reinforcement typically involves esterification modification, while PBAT tends to use silylation and graft modification. Thus, several challenges remain to be addressed in the future. First, the current preparation process for nanocellulose typically involves high energy consumption and the use of corrosive reagents, which to a certain extent limit its widespread application. Additionally, nanocellulose is generally supplied in the form of a hydrogel, and a time-consuming dehydration process is required when used to reinforce polymers, adding complexity to its application. Second, further research and verification are necessary on the biodegradability, applicability of the final products, and the sustainability of the corresponding preparation methods. It is believed that the key lies in a deeper understanding of the properties of biodegradable polymers and nanocellulose, as well as their interaction mechanisms. Based on this, more environmentally friendly, efficient, and sustainable preparation methods for nanocellulose need to be explored, while optimizing its composite technology with polymers to realize its practical application in production. Lastly, the transition from laboratory research to industrial-scale production needs to consider various factors such as production scale, cost, and environmental impact to ensure the sustainability and widespread application of the final products.

Acknowledgements

This work was supported by Tianjin Municipal Science and Technology Bureau, China (No. 23GNYZYC00004), and the Natural Science Foundation of Ningbo, China (No. 2024 J443).

[References]

[1] Jambeck J R, Geyer R, Wilcox C, Siegler T R, Perryman M, Andrady A, et al. Plastic waste inputs from land into the ocean. Science, 2015; 347(6223): 768–771.

[2] Kang P, Morrow G, Zhang X L, Wang T P, Tan Z F, Agarwal J. Systematic comparison of hydrogen production from fossil fuels and biomass resources. Int J Agric & Biol Eng, 2017; 10(6): 192–200.

[3] Mohanty A K, Vivekanandhan S, Pin J-M, Misra M. Composites from renewable and sustainable resources: Challenges and innovations. Science, 2018; 362(6414): 536–542.

[4] Zeng S H, Duan P P, Shen M X, Xue Y J, Wang Z Y. Preparation and degradation mechanisms of biodegradable polymer: A review. IOP Conference Series: Materials Science and Engineering, 2016; 137(1): 012003.

[5] Pinaeva L G, Noskov A S. Biodegradable biopolymers: Real impact to environment pollution. Science of The Total Environment, 2024; 947: 174445.

[6] Zhou L, Ke K, Yang M-B, Yang W. Recent progress on chemical modification of cellulose for high mechanical-performance Poly(lactic acid)/Cellulose composite: A review. Composites Communications, 2021; 23: 100548.

[7] Park H, He H T, Yan X, Liu X, Scrutton N S, Chen G-Q. PHA is not just a bioplastic! Biotechnology Advances, 2024; 71: 108320.

[8] Sudamrao Getme A, Patel B. A Review: Bio-fiber's as reinforcement in composites of polylactic acid (PLA). Materials Today: Proceedings, 2020; 26: 2116–2122.

[9] Sreekumar P A, Al-Harthi M A, De S K. Reinforcement of starch/polyvinyl alcohol blend using nano-titanium dioxide. Journal of Composite Materials, 2012; 46(25): 3181–3187.

[10] Calvino C, Macke N, Kato R, Rowan S J. Development, processing and applications of bio-sourced cellulose nanocrystal composites. Progress in Polymer Science, 2020; 103: 101221.

[11] Habibi Y. Key advances in the chemical modification of nanocelluloses. Chemical Society Reviews, 2014; 43(5): 1519–1542.

[12] Abdul Khalil H P S, Davoudpour Y, Islam M N, Mustapha A, Sudesh K, Dungani R, et al. Production and modification of nanofibrillated cellulose using various mechanical processes: A review. Carbohydrate Polymers, 2014; 99: 649–665.

[13] Si Y X, Lin Q Q, Zhou F., Qing J R, Luo H Z, Zhang C L, et al. The interaction between nanocellulose and microorganisms for new degradable packaging: A review. Carbohydrate Polymers, 2022; 295: 119899.

[14] Cui L, Yi L, Hegyesi N, Wang Y, Sui X, Pukánszky B. Biodegradation of poly(lactic acid)/regenerated cellulose nanocomposites prepared by the Pickering emulsion approach. Industrial Crops and Products, 2022; 187: 115411.

[15] Ventura-Cruz S, Tecante A. Nanocellulose and microcrystalline cellulose from agricultural waste: Review on isolation and application as reinforcement in polymeric matrices. Food Hydrocolloids, 2021; 118: 106771.

[16] Liu H Y, Xu T, Cai C Y, Liu K, Liu W, Zhang M, et al. Multifunctional superelastic, superhydrophilic, and ultralight nanocellulose-based composite carbon aerogels for compressive supercapacitor and strain sensor. Advanced Functional Materials, 2022; 32(26): 2113082.

[17] Xu T, Song Q, Liu K, Liu H Y, Pan J J, Liu W, et al. Nanocellulose-assisted construction of multifunctional MXene-Based aerogels with engineering biomimetic texture for pressure sensor and compressible electrode. Nano-Micro Lett, 2023; 15(1): 98.

[18] Zheng Y, Liu H, Yan L, Yang H Y, Dai L, Si C L. Lignin-based encapsulation of liquid metal particles for flexible and high-efficiently recyclable electronics. Advanced Functional Materials, 2023; 34(7): 2310653.

[19] Yang X P, Biswas S K, Han J Q, Tanpichai S, Li M C, Chen C C, et al. Surface and interface engineering for nanocellulosic advanced materials. Advanced Materials, 2021; 33(28): 2002264.

[20] Oksman K, Aitomäki Y, Mathew A P, Siqueira G, Zhou Q, Butylina S, et al. Review of the recent developments in cellulose nanocomposite processing. Composites Part A: Applied Science and Manufacturing, 2016; 83: 2–18.

[21] Ghasemlou M, Daver F, Ivanova E P, Habibi Y, Adhikari B. Surface modifications of nanocellulose: From synthesis to high-performance nanocomposites. Progress in Polymer Science, 2021; 119: 101418.

[22] Zhou Y H, Fan M Z, Chen L H. Interface and bonding mechanisms of plant fibre composites: An overview. Composites Part B: Engineering, 2016; 101: 31–45.

[23] Babu R P, O'Connor K, Seeram R. Current progress on bio-based polymers and their future trends. Progress in Biomaterials, 2013; 2(1): 8.

[24] Samir A, Ashour F H, Hakim A A A, Bassyouni M. Recent advances in biodegradable polymers for sustainable applications. NPJ Materials Degradation, 2022; 6(1): 68.

[25] Bandehali S, Sanaeepur H, Ebadi Amooghin A, Shirazian S, Ramakrishna S. Biodegradable polymers for membrane separation. Separation and Purification Technology, 2021; 269: 118731.

[26] Lunt J. Large-scale production, properties and commercial applications of polylactic acid polymers. Polymer Degradation and Stability, 1998; 59(1-3): 145–152.

[27] Hu Y, Daoud W A, Cheuk K K L, Lin C S K. Newly developed techniques on polycondensation, ring-opening polymerization and polymer modification: Focus on poly(lactic acid). Materials, 2016; 9(3): 133.

[28] Eubeler J P, Bernhard M, Knepper T P. Environmental biodegradation of synthetic polymers II. Biodegradation of different polymer groups. TrAC Trends in Analytical Chemistry, 2010; 29(1): 84–100.

[29] Barbier-Baudry D, Brachais L, Cretu A, Gattin R, Loupy A, Stuerga D. Synthesis of polycaprolactone by microwave irradiation - An interesting route to synthesize this polymer via green chemistry. Environmental Chemistry Letters, 2003; 1: 19–23.

[30] Rasal R M, Janorkar A V, Hirt D E. Poly(*lactic acid*) modifications. Progress in Polymer Science, 2010; 35(3): 338–356.

[31] Xing Q, Zhang X Q, Dong X, Liu G M, Wang D J. Low-molecular weight aliphatic amides as nucleating agents for poly (L-lactic acid): Conformation variation induced crystallization enhancement. Polymer, 2012; 53(11): 2306–2314.

[32] Meng D-C, Shen R, Yao H, Chen J-C, Wu Q, Chen G-Q. Engineering the diversity of polyesters. Current Opinion in Biotechnology, 2014; 29: 24–33.

[33] Sirohi R, Prakash Pandey J, Kumar Gaur V, Gnansounou E, Sindhu R. Critical overview of biomass feedstocks as sustainable substrates for the production of polyhydroxybutyrate (PHB). Bioresource Technology, 2020; 311: 123536.

[34] Rafiqah S A, Khalina A, Harmaen A S, Tawakkal I A, Zaman K, Asim M, et al. A Review on Properties and Application of Bio-Based Poly(Butylene Succinate). Polymers (Basel), 2021; 13(9): 1436.

[35] Palsikowski P A, Kuchnier C N, Pinheiro I F, Morales A R. Biodegradation in soil of PLA/PBAT blends compatibilized with chain extender. Journal of Polymers and the Environment, 2018; 26: 330–341.

[36] Zhou S-Y, Huang H-D, Ji X, Yan D-X, Zhong G-J, Hsiao B S, et al. Super-robust polylactide barrier films by building densely oriented lamellae incorporated with ductile in situ nanofibrils of poly(butylene adipate-co-terephthalate). ACS Applied Materials & Interfaces, 2016; 8(12): 8096–8109.

[37] Shung A K, Timmer M D, Jo S, Engel P S, Mikos A G. Kinetics of poly(propylene fumarate) synthesis by step polymerization of diethyl fumarate and propylene glycol using zinc chloride as a catalyst. Journal of Biomaterials Science, Polymer Edition, 2002; 13(1): 95–108.

[38] Raquez J-M, Habibi Y, Murariu M, Dubois P. Polylactide (PLA)-based nanocomposites. Progress in Polymer Science, 2013; 38(10-11): 1504–1542.

[39] da Costa F A T, Parra D F, Cardoso E C L, Güven O. PLA, PBAT, Cellulose nanocrystals (CNCs), and their blends: Biodegradation, compatibilization, and nanoparticle interactions. Journal of Polymers and the Environment, 2023; 31(11): 4662–4690.

[40] Aydemir D, Gardner D J. Biopolymer blends of polyhydroxybutyrate and polylactic acid reinforced with cellulose nanofibrils. Carbohydrate Polymers, 2020; 250: 116867.

[41] Jeon H, Lee M, Yun S, Kang D, Park K-h, Choi S, et al. Fabrication and characterization of 3D-printed biocomposite scaffolds based on PCL and silanated silica particles for bone tissue regeneration. Chemical Engineering Journal, 2019; 360: 519–530.

[42] Fadaie M, Mirzaei E, Geramizadeh B, Asvar Z. Incorporation of nanofibrillated chitosan into electrospun PCL nanofibers makes scaffolds with enhanced mechanical and biological properties. Carbohydrate Polymers, 2018; 199: 628–640.

[43] Cai Z Y, Wan Y, Becker M L, Long Y-Z, Dean D. Poly(propylene fumarate)-based materials: Synthesis, functionalization, properties, device fabrication and biomedical applications. Biomaterials, 2019; 208: 45–71.

[44] Kasper F K, Tanahashi K, Fisher J P, Mikos A G. Synthesis of poly(propylene fumarate). Nature Protocols, 2009; 4(4): 518–525.

[45] Liu W, Liu K, Du H S, Zheng T, Zhang N, Xu T, et al. Cellulose nanopaper: fabrication, functionalization, and applications. Nano-Micro Lett, 2022; 14(1): 104.

[46] Li W, Zhu L Y, Xu Y, Wang G H, Xu T, Si C L. Lignocellulose-Mediated functionalization of liquid metals towards the frontiers of multifunctional materials. Advanced Materials, 2024; 36: 2415761.

[47] Li W, Xu Y, Wang G H, Xu T, Si C L. Design and functionalization of lignocellulose-derived silicon-carbon composites for rechargeable batteries. Advanced Energy Materials, 2024; 14: 2403593.

[48] Nechyporchuk O, Belgacem M N, Bras J. Production of cellulose nanofibrils: A review of recent advances. Industrial Crops and Products, 2016; 93: 2–25.

[49] Lin N, Dufresne A. Nanocellulose in biomedicine: Current status and future prospect. European Polymer Journal, 2014; 59: 302–325.

[50] Wang H, Du H S, Liu K, Liu H Y, Xu T, Zhang S Y, et al. Sustainable preparation of bifunctional cellulose nanocrystals via mixed H2SO4/formic acid hydrolysis. Carbohydrate Polymers, 2021; 266: 118107.

[51] Liu W, Zhang S Y, Liu K, Yang H B, Lin Q Y, Xu T, et al. Sustainable preparation of lignocellulosic nanofibrils and cellulose nanopaper from poplar sawdust. Journal of Cleaner Production, 2023; 384: 135582.

[52] Ifuku S, Nogi M, Abe K, Handa K, Nakatsubo F, Yano H. Surface modification of bacterial cellulose nanofibers for property enhancement of optically transparent composites: Dependence on Acetyl-Group DS. Biomacromolecules, 2007; 8(6): 1973–1978.

[53] Filson P B, Dawson-Andoh B E, Schwegler-Berry D. Enzymatic-mediated production of cellulose nanocrystals from recycled pulp. Green Chemistry, 2009; 11(11): 1808–1814.

[54] Gomri C, Cretin M, Semsarilar M. Recent progress on chemical modification of cellulose nanocrystal (CNC) and its application in nanocomposite films and membranes-A comprehensive review. Carbohydrate Polymers, 2022; 294: 119790.

[55] Ahankari S S, Subhedar A R, Bhadauria S S, Dufresne A. Nanocellulose in food packaging: A review. Carbohydrate Polymers, 2021; 255: 117479.

[56] Xu T, Du H S, Liu H Y, Liu W, Zhang X Y, Si C L, et al. Advanced nanocellulose-based composites for flexible functional energy storage devices. Advanced Materials, 2021; 33(48): 2101368.

[57] Li Q, Yang F L, Zheng G X, Guan Z J. Effects of urea ammonia pretreatment on the batch anaerobic fermentation efficiency of corn stovers. Int J Agric & Biol Eng, 2019; 12(4): 169–173.

[58] Liu K, Wang Y X, Liu W, Zheng C Y, Xu T, Du H S, et al. Bacterial cellulose/chitosan composite materials for biomedical applications. Chemical Engineering Journal, 2024; 494: 153014.

[59] Hao X L, Xu J J, Zhou H Y, Tang W, Li W J, Wang Q W, et al. Interfacial adhesion mechanisms of ultra-highly filled wood fiber/polyethylene composites using maleic anhydride grafted polyethylene as a compatibilizer. Materials & Design, 2021; 212: 110182.

[60] Nagalakshmaiah M, Pignon F, El Kissi N, Dufresne A. Surface adsorption of triblock copolymer (PEO-PPO-PEO) on cellulose nanocrystals and their melt extrusion with polyethylene. RSC Advances, 2016; 6(70): 66224–66232.

[61] Ren Q, Wu M H, Wang L, Zheng W G, Hikima Y, Semba T, et al. Cellulose nanofiber reinforced poly (lactic acid) with enhanced rheology, crystallization and foaming ability. Carbohydrate Polymers, 2022; 286: 119320.

[62] Jamaluddin N, Kanno T, Asoh T-A, Uyama H. Surface modification of cellulose nanofiber using acid anhydride for poly(lactic acid) reinforcement. Materials Today Communications, 2019; 21: 100587.

[63] Hu F, Lin N, Chang P R, Huang J. Reinforcement and nucleation of acetylated cellulose nanocrystals in foamed polyester composites. Carbohydrate Polymers, 2015; 129: 208–215.

[64] Shojaeiarani J, Bajwa D S, Hartman K. Esterified cellulose nanocrystals as reinforcement in poly(lactic acid) nanocomposites. Cellulose, 2019; 26(4): 2349–2362.

[65] Liu S L, Zhang Q, Gou S H, Zhang L L, Wang Z. Esterification of cellulose using carboxylic acid-based deep eutectic solvents to produce high-yield cellulose nanofibers. Carbohydrate Polymers, 2021; 251: 117018.

[66] Mugwagwa L R, Chimphango A F A. Enhancing the functional properties of acetylated hemicellulose films for active food packaging using acetylated nanocellulose reinforcement and polycaprolactone coating. Food Packaging and Shelf Life, 2020; 24: 100481.

[67] Celebi H, Ilgar M, Seyhan A T. Evaluation of the effect of isocyanate modification on the thermal and rheological properties of poly(ε-caprolactone)/cellulose composites. Polymer Bulletin, 2021; 79(7): 4941–4955.

[68] Fijoł N, Aguilar-Sánchez A, Ruiz-Caldas M-X, Redlinger-Pohn J, Mautner A, Mathew A P. 3D printed polylactic acid (PLA) filters reinforced with polysaccharide nanofibers for metal ions capture and microplastics separation from water. Chemical Engineering Journal, 2023; 457: 141153.

[69] Li L Y, Chen Y, Yu T X, Wang N, Wang C S, Wang H P. Preparation of polylactic acid/TEMPO-oxidized bacterial cellulose nanocomposites for 3D printing via Pickering emulsion approach. Composites Communications, 2019; 16: 162–167.

[70] Luo J, Ghaffar S, Chen W C, Gao S S, Jiang Y J. Integration of inorganic ionic oligomers and nanocellulose within PVA networks: A degradable and green nanocomposite with self-healable property and high mechanical strength in a wet state. Polymer, 2023; 284: 126307.

[71] Espinosa E, Bascón-Villegas I, Rosal A, Pérez-Rodríguez F, Chinga-Carrasco G, Rodríguez A. PVA/(ligno) nanocellulose biocomposite films. Effect of residual lignin content on structural, mechanical, barrier and antioxidant properties. International Journal of Biological Macromolecules, 2019; 141: 197–206.

[72] Jiang G, Yu L, Zhang M D, Wang F, Zhang S D. Poly(propylene carbonate)/poly(3-hydroxybutyrate)-based bionanocomposites reinforced with cellulose nanocrystal for potential application as a packaging material. Polymers for Advanced Technologies, 2019; 31(4): 853–863.

[73] Lee H, You J, Jin H-J, Kwak H W. Chemical and physical reinforcement behavior of dialdehyde nanocellulose in PVA composite film: A comparison of nanofiber and nanocrystal. Carbohydrate Polymers, 2020; 232: 115771.

[74] Jin K Y, Tang Y J, Zhu X M, Zhou Y M. Polylactic acid based biocomposite films reinforced with silanized nanocrystalline cellulose. International Journal of Biological Macromolecules, 2020; 162: 1109–1117.

[75] Kargarzadeh H, Sheltami R M, Ahmad I, Abdullah I, Dufresne A. Cellulose nanocrystal reinforced liquid natural rubber toughened unsaturated polyester: Effects of filler content and surface treatment on its morphological, thermal, mechanical, and viscoelastic properties. Polymer, 2015; 71: 51–59.

[76] Zhang P B, Lu Y D, Fan M M, Jiang P P, Dong Y M. Modified cellulose nanocrystals enhancement to mechanical properties and water resistance of vegetable oil-based waterborne polyurethane. Journal of Applied Polymer Science, 2019; 136(47): 48228.

[77] Dhali K, Daver F, Cass P, Field M R, Adhikari B. Development and characterisation of poly(butylene adipate-co-terephthalate)- silane modified cellulose nanocrystals composite materials and films. Journal of

Polymers and the Environment, 2023; 31(10): 4506–4521.

[78] Goussé C, Chanzy H, Excoffier G, Soubeyrand L, Fleury E. Stable suspensions of partially silylated cellulose whiskers dispersed in organic solvents. Polymer, 2002; 43(9): 2645–2651.

[79] Goussé C, Chanzy H, Cerrada M L, Fleury E. Surface silylation of cellulose microfibrils: preparation and rheological properties. Polymer, 2004; 45(5): 1569–1575.

[80] Sai H Z, Fu R, Xing L, Xiang J H, Li Z Y, Li F, et al. Surface modification of bacterial cellulose aerogels' web-like skeleton for oil/water separation. ACS Applied Materials & Interfaces, 2015; 7(13): 7373–7381.

[81] Stenstad P, Andresen M, Tanem B S, Stenius P. Chemical surface modifications of microfibrillated cellulose. Cellulose, 2008; 15(1): 35–45.

[82] Wang Z R, Jin K X, Lim K H, Liu P W, Lu D, Yang X, et al. Biodegradable poly(butylene adipate-co-terephthalate) nanocomposites reinforced with in situ fibrillated nanocelluloses. ACS Sustainable Chemistry & Engineering, 2023; 11(27): 9947–9955.

[83] Yin Y Y, Tian X Z, Jiang X, Zhu P. Modification of cellulose nanocrystals via surface-initiated ARGET ATRP and their reinforcement of poly(lactic acid)-based biocomposites. Industrial Crops and Products, 2022; 188: 115575.

[84] Barbosa R F S, Souza A G, Rosa D S. Acetylated cellulose nanostructures as reinforcement materials for PBAT nanocomposites. Polymer Composites, 2020; 41(7): 2841–2854.

[85] Niu W D, Guo Y F, Huang W, Song L L, Xiao Z F, Xie Y J, et al. Aliphatic chains grafted cellulose nanocrystals with core-corona structures for efficient toughening of PLA composites. Carbohydrate Polymers, 2022; 285: 119200.

[86] Chuensangjun C, Kitaoka T, Chisti Y, Sirisansaneeyakul S. Chemo-enzymatic preparation and characterization of cellulose nanofibers-graft-poly(lactic acid)s. European Polymer Journal, 2019; 114: 308–318.

[87] Kwak H, Kim H, Park S-A, Lee M, Jang M, Park S B, et al. Biodegradable, water-resistant, anti-fizzing, polyester nanocellulose composite paper straws. Advanced Science, 2022; 10(1): 2205554.

[88] Carlsson L, Ingverud T, Blomberg H, Carlmark A, Larsson P T, Malmström E. Surface characteristics of cellulose nanoparticles grafted by surface-initiated ring-opening polymerization of ε-caprolactone. Cellulose, 2015; 22(2): 1063–1074.

[89] Lalanne-Tisne M, Mees M A, Eyley S, Zinck P, Thielemans W. Organocatalyzed ring opening polymerization of lactide from the surface of cellulose nanofibrils. Carbohydrate Polymers, 2020; 250: 116974.

[90] Lönnberg H, Larsson K, Lindstrom T, Hult A, Malmstrom E. Synthesis of polycaprolactone-grafted microfibrillated cellulose for use in novel bionanocomposites-influence of the graft length on the mechanical properties. ACS Applied Materials & Interfaces, 2011; 3(5): 1426–1433.

[91] Kim J-K, Bandi R, Dadigala R, Hai L V, Han S-Y, Kwon G-J, et al. Esterification of nanofibrillated cellulose using lauroyl chloride and its composite films with polybutylene succinate. BioResources, 2023; 18(4): 7143–7153.

[92] Wu C Q, Zhang X Z, Wang X H, Gao Q W, Li X N. Surface modification of cellulose nanocrystal using succinic anhydride and its effects on poly(butylene succinate) based composites. Cellulose, 2019; 26(5): 3167–3181.

[93] Pal N, Banerjee S, Roy P, Pal K. Reduced graphene oxide and PEG-grafted TEMPO-oxidized cellulose nanocrystal reinforced poly-lactic acid nanocomposite film for biomedical application. Materials Science & Engineering C-Materials for Biological Applications, 2019; 104: 109956.

[94] Averianov I V, Stepanova M A, Gofman I V, Nikolaeva A L, Korzhikov-Vlakh V A, Karttunen M, et al. Chemical modification of nanocrystalline cellulose for improved interfacial compatibility with poly(lactic acid). Mendeleev Communications, 2019; 29(2): 220–222.

[95] Mai V-D, Kang D, Kim Y, Jang Y, Min J, Han J-h, et al. Preparation and environmental analysis of biodegradable polylactic acid and modified cellulose nanofiber composites. Journal of Industrial and Engineering Chemistry, 2024; 130: 401–411.

[96] Lai L, Wang S L, Li J X, Liu P W, Wu L B, Wu H Q, et al. Stiffening, strengthening, and toughening of biodegradable poly(butylene adipate-co-terephthalate) with a low nanoinclusion usage. Carbohydrate Polymers, 2020; 247: 116687.

[97] Leja K, Lewandowicz G. Polymer biodegradation and biodegradable polymers-a review. Polish Journal of Environmental Studies, 2010; 19(2): 255–266.

[98] Zheng G X, Lu Z X, Li J, Ai S, Sun Y. Screening and performance of L-14, a novel, highly efficient and low temperature-resistant cellulose-degrading strain. Int J Agric & Biol Eng, 2020; 13(1): 247–254.

[99] Sucinda E F, Abdul Majid M S, Ridzuan M J M, Cheng E M, Alshahrani H A, Mamat N. Development and characterisation of packaging film from Napier cellulose nanowhisker reinforced polylactic acid (PLA) bionanocomposites. International Journal of Biological Macromolecules, 2021; 187: 43–53.

[100] Xu A, Wang Y X, Gao J, Wang J J. Facile fabrication of a homogeneous cellulose/polylactic acid composite film with improved biocompatibility, biodegradability and mechanical properties. Green Chemistry, 2019; 21(16): 4449–4456.

[101] Morelli C L, Belgacem N, Bretas R E S, Bras J. Melt extruded nanocomposites of polybutylene adipate-co-terephthalate (PBAT) with phenylbutyl isocyanate modified cellulose nanocrystals. Journal of Applied Polymer Science, 2016; 133(34): 43678.

[102] Chen Y, Lu T T, Li L Y, Zhang H Y, Wang H P, Ke F Y. Fully biodegradable PLA composite with improved mechanical properties via 3D printing. Materials Letters, 2023; 331: 133543.

[103] Mendoza D J, Browne C, Raghuwanshi V S, Mouterde L M M, Simon G P, Allais F, et al. Phenolic ester-decorated cellulose nanocrystals as UV-absorbing nanoreinforcements in polyvinyl alcohol films. ACS Sustainable Chemistry & Engineering, 2021; 9(18): 6427–6437.

[104] Montero Y, Souza A G, Oliveira É R, Rosa D d S. Nanocellulose functionalized with cinnamon essential oil: A potential application in active biodegradable packaging for strawberry. Sustainable Materials and Technologies, 2021; 29: e00289.

[105] Yang Y C, Zhong M Y, Wang W Q, Lu N, Gou Y K, Cai W L, et al. Engineering biodegradable bacterial cellulose/polylactic acid multi-scale fibrous membrane via co-electrospinning-electrospray strategy for efficient, wet-stable, durable PM0.3 filtration. Separation and Purification Technology, 2025; 352: 128143.

[106] Zhou H, Yan L, Tang D X, Xu T, Dai L, Li C Y, et al. Solar-driven drum-type atmospheric water harvester based on bio-based gels with fast adsorption/desorption kinetics. Advanced Materials, 2024; 36(32): 2403876.

[107] Yi Q, Lu S, Fan Y T, Cheng D H, Wang X M, Cheng S L, et al. Preparation and adsorption performance of cellulose nanofibrils/polyvinyl alcohol composite gel spheres with millimeter size. Carbohydrate Polymers, 2022; 277: 118850.