Recently Progress on Polylactide/Nanocellulose Nanocomposites

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Abstract. The development of renewable resources is a trend in the future. Polylactide (PLA), as one member of bio-polymers, has obtained a widely focus in industry and academy because of its renewability, biodegradability, biocompatibility and good thermomechanical properties. PLA is used in a wide variety of applications such as biomedical, food packaging, electrical and electronic equipment, and the automotive industry. However, PLA still has some shortcomings, such as lower heat distortion temperature, slower crystallization rate, lower thermal resistance, etc. These shortcomings also limit the further widespread use of PLA. One effective method to expand and improve these properties of PLA is adding nanofillers. This review summarizes and describes the role of nanocellulose as a filler in the modification of PLA matrix and some of the problems faced.

Key words: Polylactide/ Nanocellulose, Nanocomposites, Bio-polymers.

1. Introduction
Bio-polymers which are obtained from renewable resources are widely considered as promising alternatives to traditional petro-polymers because they fulfill current environmental concerns in terms of environmental pollution [1, 2]. As one of the members of bio-polymer, poly(lactic acid) (PLA) is a leader biopolymer due to its attractive mechanical properties, reproducibility and biodegradability [3], with which a Young modulus of ~3 GPa, a strength of 50–70 MPa, an elongation at break of ~4 %, and an impact strength close to 2.5 kJ/m [2, 4]. These mechanical properties, particularly the Young’s modulus, are better than the most of commodity polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET), leading it as an excellent candidate for exchanging commodity polymers in short-time packaging. However, the low impact strength of PLA limits the widely application. [3] Furthermore, PLA shows poor crystallization ability, which largely limiting its industrial implementation in various applications. [5] One way usually developed to enhance both the crystallization ability and impact strength over the past years is incorporating reinforcements within the polymer matrix, yielding so-called nanocomposite materials [6, 7]. Much of different types of nanofillers have been incorporated into PLA matrix as an enchant agent to modify its thermo- and mechanical properties as well as to provide additional functionalities like conductivity and flame retardancy.

Nanocomposites refer to the fillers with at least one dimension at the nanometer level. Lots of researches have been carried out about polymeric nanocomposites due to their properties substantially improved at very low nanofiller loadings [8]. Environmentally friendly nanocomposites are the key
direction for future nano-material development. Nanocellulose, as a renewable green material extracted from organisms, has received extensive attention in recent years. Cellulose has good mechanical properties and is the main material that constitutes the cell wall of plants, which can improve the resistance to deformation of key parts. Cellulose has a wide range of sources, low prices, and no pollution to the environment, so as to one of the ideal fillers for the formation of polymer composites. Since nanocellulose is mostly fibrous, when it is used as a filler, it can be laterally separated from the entire amorphous portion present on its axis, resulting in defect-free rod-shaped nanoparticles. According to the aggregate structure of the rod-shaped nanoparticles, it can be classified into cellulose nanocrystals (CN) and nanofibrillated cellulose (NFC). Their morphology are shown in Figure 1 and Figure 2, respectively. Among them, nanofibrillated cellulose can also be biosynthesized by microorganisms, and is known as bacterial cellulose (BC). This paper will summarize recent research on PLA-based nanocellulose nanocomposites and look forward to future opportunities.

**Figure 1.** TEM micrographs of a dilute suspension of NFCs obtained from wood fibers by mechanical processing that was employed in conjunction with (a) enzymatic treatment [9]; (b) TEMPO-mediated oxidation [10]; (c) carboxymethylation pretreatment [11]; (d) NFCs extracted from Opuntia ficus-indica [12].

**Figure 2.** TEM images of dried dispersion of cellulose nanocrystals derived from (a) tunicate [13], (b) bacterial [13], (c) ramie [14] and (d) sisal [15].
2. PLA/nanocellulose nanocomposites

Nanocellulose substrates have high surface area, low density, high mechanical strength and controllable nanoscale size, which has attracted great interest in the preparation of high performance nanocomposites. A larger number of studies have shown that nanocrystalline cellulose has comparable or even better mechanical properties than other materials. In addition, nanocellulose crystals have some advantages not found in other types of fillers, such as being more readily available, and renewable and biodegradable. Nanocellulose fillers including NFC, CN and BC, have been incorporated into a variety of polymer matrices such as PLA. However, obtaining good dispersion of the filler in the PLA matrix remains one of the major challenges in the preparation of nanocomposites. Nanocellulose has a large number of hydroxyl groups on the surface, so its good hydrophilicity makes them poorly dispersible in hydrophobic matrices such as PLA or common non-polar solvents, so it is very easy to induce nanocellulose particles aggregation phenomenon in the PLA matrix. In addition, due to the hydrogen bond network formed by a large number of hydroxyl groups and hydroxyl groups present on the surface of the nanocellulose, irreversible aggregation of the nanocellulose substrate is also caused upon drying. Therefore, they usually remain dispersed in an aqueous medium or a polar solvent after preparation. At present, different processing methods have been reported, and several chemical strategies have been developed to adjust the interfacial compatibility between PLA and nanocellulose substrates. However, the final results and uses of nanocellulose-based PLA composites have rarely been reported.

2.1. PLA/CNs nanocomposites

The first report on the preparation of PLA-based nanocomposites for nanocellulose as a filler was to inject the aqueous suspension of PLA into the PLA melt during extrusion. However, due to the strong aggregation properties of NFC, the lack of compatibility with PLA matrix, the hydrolytic degradation of PLA induced by the presence of water, and the fact that no thermal or mechanical properties of the final product have been studied in this attempt, it is suspected that the first report is mediocre. [16] Oksman et al. [17] It has recently been reported that a mixture of lithium chloride (LiCl) and N,N-dimethylacetamide (DMAc) is useful to swell and partially separate CN, and finally the suspension is extruded to the PLA melt during the extrusion process. A composite material in which CNs are well dispersed in a PLA matrix can be obtained. However, the disadvantage of this study is that DMAc / LiCl appears to cause degradation of the composite at high processing temperatures. One of the improvement methods of this processing strategy is to use polyvinyl alcohol (PVOH) as a processing aid [18], and mix PVOH with PLA before extrusion or directly into the extruder by mixing PVOH with CN suspension. However, in both cases, the resulting nanocomposites showed poor mechanical properties, mainly due to the phase separation structure of the PLA and PVOH phases, where PLA is the continuous phase and PVOH is the discontinuous phase. The CN is mainly located in the discontinuous phase PVOH, which greatly limits the load transfer between the nanofiller and the PLA matrix. To some degree, this strategy is not conducive to the improvement of the comprehensive mechanical properties. In addition to this, it is also possible to coat the surface of the CNs with an anionic surfactant and then incorporate the surface-modified CNs into the PLA melt in a dry state during the extrusion of the PLA in order to improve the CNs in the PLA matrix. [19] The dispersing ability of the anionic surfactant is usually composed of a phosphate having an alkylphenol tail. However, when the surfactant content is low, the dispersion state of CNs in the PLA matrix is not improved. As the surfactant content increases, the dispersion of CNs in the PLA matrix becomes good, but excess surfactant tends to cause significant thermal degradation of the PLA matrix at processing temperatures. The mechanical properties of the reinforced nanocomposite are improved compared to unreinforced nanocomposites. Further studies have shown that the use of solvent casting instead of extrusion to combine surfactant-modified CN with the same surfactant into PLA results in a better dispersion state. However, the thermomechanical properties of the PLA composites prepared by this method have decreased, although the results of TGA indicate that the obtained nanocomposites can still exist stably at 220 °C, but the DMA test results (as shown in Figure 3) show that the excess surfactant can reduce the composite materials. The storage modulus is
mainly due to the very strong interaction between PLA and surfactant, but the interaction between CN and surfactant is relatively weak, so reinforcement is not achieved to some extent. [20]

![Figure 3](image)

**Figure 3.** Storage modulus curves and tan δ peaks from DMTA analysis. (a) PLA, PLA/CNW and PLA/B-CNW (b) PLA, PLA/S and PLA/S-CNW. [20]

On the other hand, the surfactant-modified CNs significantly enhanced the crystallization nucleation ability of PLA, which to some extent highlighted the influence of crystal and its surface modification on the thermal and mechanical properties of nanocomposites. Studies have shown that although aggregates are still present on very small scales, CN promotes nucleation and subsequent crystallization of PLA more efficiently in composites of amorphous PLA than in composites [21-23] of crystalline PLA. In addition to mechanical properties, the study also found that, when the content of CNs is more than 3 wt%, not only the crystallinity of PLA is significantly improved, but also the water and oxygen permeability of PLA nanocomposites can be significantly improved, which can be increased to 82 % and 90 % [22]. It is worth noting here that the presence of CNs does not impair the hydrolytic degradation of PLA nanocomposites as expected, but instead causes a strong delay. The reason is the physical barrier effect of highly crystalline CN, which inhibits water absorption and thus delays the hydrolytic degradation of the bio-nanocomposite. The results of the study indicate that CNs may control biodegradability and extend the life of PLA by incorporating a small amount of nanocellulose. [24]

2.2. **PLA/NFC nanocomposites**

NFC is also one of the main green fillers for the preparation of reinforced PLA nanocomposites. Solution casting can generally be used to prepare high levels of NFC PLA/NFC masterbatch, followed by melt blending with a PLA matrix by twin screw extrusion using a strategy of diluting the wood. [25] That is, a PLA nanocomposite with a relatively good NFC dispersion state and good mechanical properties can be obtained by a two-step process. Acetone, chloroform, etc. are common organic solvents in industry and laboratories (as shown in Figure 4). Unmodified NFC can be pre-mixed with PLA using a low-boiling organic solvent such as acetone. After stirring, the organic solvent can be removed and dried.
The NFC uniformly disperses the nanocomposite in the PLA, and finally the sheet is prepared by means of hot pressing or the like. [26] The well-dispersed NFC particles reinforced the PLA matrix, which increased the Young’s modulus and tensile strength of the PLA by 40 % and 25 %, respectively, and the yield strain did not decrease when the content of the nanofiller was 10 wt%. Further studies have found that the storage modulus of the composite remains constant above the $T_g$ of the PLA matrix. In addition, the authors also found that the addition of NFC accelerates the crystallization of fully amorphous PLA [27] and has the same ability to promote PLA crystal nucleation as CNs. [28] And the promotion effect exhibited in the amorphous PLA matrix is significantly better than that of the semi-crystalline PLA matrix. Recently, the same group of researchers further found that when NFC is combined with another nucleating agent, zinc phenylphosphonate (PPA-Zn), the combination of the two has a synergistic effect on the crystallization and mechanical properties of the PLA composite. The mechanism of synergy is: The effective nucleation of PPA-Zn accelerates the crystallization of PLA and the enhancement of NFC, thus providing higher strength and hardness for the composite. This synergistic effect greatly increases the dimensional stability of the material, so that the composite is not deformed even when the composite is injection molded at a high temperature (95 °C) for a holding time of 10 s [29].

![Typical stress–strain curves comparing the solvent method, direct mixing method compounding, and neat PLA.](image)

**Figure 4.** Typical stress–strain curves comparing the solvent method, direct mixing method compounding, and neat PLA. [26]

![Scanning electron micrographs of a MFC/PLA sheet containing 70 wt% MFC. The network of tiny MFC fibrils is uniformly adhered to the thick PLA fibers. Arrows point to PLA fibers.](image)

**Figure 5.** Scanning electron micrographs of a MFC/PLA sheet containing 70 wt% MFC. The network of tiny MFC fibrils is uniformly adhered to the thick PLA fibers. Arrows point to PLA fibers. [30]
In addition, Nakagaito et al. [30] developed a new manufacturing process similar to papermaking for the production of NFC-reinforced PLA nanocomposites (as shown in Figure 5). Since this method has a significant advantage of high productivity and rapid dehydration, this method can be industrially mass-produced. The thin-plate composites produced by this method have excellent mechanical properties. Studies have shown that the modulus, strength and strain of the composites at break are linearly increased with the NFCs content. Furthermore, slight modifications in this process are also enabled direct mixing of the different components allows for good NFC dispersion in the PLA in the bio-nanocomposite, improving the mechanical properties of the composite even at high NFC levels. The greater the content of NFC, the stronger the composite will become and the more sensitive it becomes to defects. NFC nanoparticles can also play a good role in bio-based nanocomposites. For example, the formation of a strong NFC network of NFC particles in a PLA matrix can improve the thermal stability of the composite. Since the surface of the NFC has a large amount of hydroxyl groups, the NFC can carry a part of water, and the water carried by the NFC can be used as a natural foaming agent to prepare a foam structure of the PLA-based composite material. [31] Studies have shown that due to the high activity of hydroxyl groups, NFC can be modified by carboxymethylation or acetylation to change the NFC hygroscopicity, and the amount of water present in the starting system can be adjusted under different humidity conditions. Carboxymethylated NFC can provide a higher water content, making it possible to tailor the density of biocomposite foams. For example, 9.6 wt% water and 8.3 wt% can be used to prepare foams with a density of 0.68 g/cm$^3$ and 0.84 g/cm$^3$, respectively. However, studies have found that only water adsorbed on the fibrils can act as an effective blowing agent.

It has been reported that electrospinning is a useful process for producing PLA nanocomposites in which the filler is a nanocellulose matrix in the form of fibers. For example, the PLA/CNs nanocomposite fiber can be electrospun at a high temperature from a solution of PLA in N-N-dimethylformamide (DMF) containing suspended cellulose nanocrystals, thereby obtaining a well-dispersed PLA/CNs nanocomposite fiber. The fibrous nanocomposites prepared by the electrospinning method have a smooth morphology and a uniform nanometer diameter [32] even at a filler content of up to 10 wt%. The increase in the CNs content caused a slight decrease in the fiber diameter, but the elongation at break of the electrospun nonwoven fabric decreased. Fine research has found that the distribution of CN in the fibers obtained by electrospinning is not very uniform, and the amount of CN available on the surface is larger than the amount of CN inside, indicating that there is no adhesion between CN and PLA in the fiber. Fortunately, despite the lack of compatibility, CN can act as a nucleation site during electrospinning, resulting in an increase in crystallinity of the electrospun PLA nanocomposite as the CN content increases. Due to the reduction in the diameter of the electrospun fiber and the increase in crystallinity, the strength of the electrospun nonwoven fabric can be achieved by adding CNs to the PLA. Liu et al. used a similar method to prepare uniform smooth fibers with an average diameter of 300 nm, and the mechanical properties of the composites were greatly improved. [33]

2.3. PLA/BC nanocomposites

In order to achieve good dispersion of nanocellulose in the PLA matrix and increase the compatibility of the nanofiller with the polymer matrix, the researchers also tried to use covalent chemical functionalization of nanocellulose. Several chemical modifications that have been successfully implemented include esterification, silanization, and polymer grafting etc. Lee et al. [34] have extensively studied the esterification of organic acids with different chain lengths (C2 to C12) with BC nanofibers in order to adjust their hydrophobic equilibrium as shown in Figure 6. When the chain length of the organic acid used for the modification is larger than C2, the tensile modulus and tensile strength of the nanocomposite will be significantly improved after the esterified BC filler and the PLA matrix are combined by the twin-screw extrusion technique. However, when the BC particles are modified by the acetylation of an organic acid of the same chain length (chain length of C2), the ester bond will be degraded during the twin-screw extrusion process. Further release of the acetic acid molecule will catalyze the degradation of the PLA matrix, causing a decrease in the molecular weight of the PLA,
further impairing the mechanical properties of the final nanocomposite. Interestingly, when the acetylation reaction occurs under moderate conditions, the degree of acetylation is significantly reduced, and not only good dispersion of BC nanofibers in PLA can be obtained. Moreover, no degradation was observed in the nanocomposite produced by the twin-screw extrusion processing at a high temperature of 190 °C. A significant increase in elastic and Young’s modulus and tensile strength (increased by about 100%, 40% and 25%, respectively) at a very low nanofiller content demonstrates a significant improvement in thermal and mechanical properties.

![Figure 6. Scanning electron micrographs of: (a) neat BC, (b) C2-BC, (c) C6-BC and (d) C12-BC. [34]](image)

Moreover, these nanocomposites exhibit interesting and very meaningful physical characteristics such as humidity insensitivity, high transparency, and resistance to aging. Studies have shown that when acetylated NFC [35] or acetylated CNs [36] is added to the PLA matrix by casting-evaporation techniques at room temperature, the dispersion of nanoparticles is improved due to the good interfacial adhesion between the surface of the nanoparticles and the PLA matrix. The state of dispersion in the polymer matrix ultimately results in the material not only resisting degradation, but also significantly enhancing the mechanical properties of the composite. Another example is the incorporation of maleic anhydride-modified BC nanofibers into a PLA matrix by solution casting, followed by compression to prepare composites. The composites prepared by this method also have excellent mechanical properties [37]. In addition, the partial silanization process of CNs extracted from cotton was studied. [38] The CNs extracted from cotton are first reacted with n-dodecyldimethylchlorosilane. The purpose of this method is to obtain good dispersion of CN in the composite. It was found that when the silanized CNs content is only 1%, the crystallization rate of PLA will be significantly increased as shown in Figure 7. In contrast, unmodified CNs have limited impact on the crystallization ability of PLA. Furthermore, studies have found that the increase in crystallinity can effectively improve the tensile modulus and strength of the composite, but the increase in crystallinity is not conducive to the increase in elongation at break.
In addition, the researchers also attempted to adjust the compatibility between nanocellulose and PLA by silanizing the surface of NFC fibers and CN fibers with 3-amino propyl triethoxysilane. [39] Then the PLA-based nanocomposites were prepared by twin-screw extrusion processing, but the final mechanical properties were only slightly increased. This may be due to the aminolysis reaction of the amine groups during high-temperature processing, which caused the degradation of the PLA molecular chains. Recent studies have found that CNs can be directly combined with silanes having different functional groups (i.e. alkyl, amino, methacryloxy) [40] after extraction. The reaction process is simple and easy to control, and can be efficiently carried out in an aqueous medium at room temperature. After the reaction product is freeze-dried, the obtained silylated CN can be successfully incorporated into the PLA matrix by twin-screw extrusion. It is found that there is no change in nanostructures and a decrease in molecular weight even in the high-temperature twin-screw extrusion process. In addition, Li et al. [41] successfully grafted epoxy-terminated polylactide- glycidyl methacrylate copolymer onto the surface of BC nanofibers by surface grafting. The nanofibers obtained by this method showed good dispersibility in the PLA matrix, but unfortunately the study did not report any mechanical properties. Furthermore, by means of a "grafting" method, a polycaprolactone (PCL) chain can be grown from the surface of the CNs by microwave-assisted ring-opening polymerization, and then the surface-modified CNs fibers are dispersed into the PLA matrix [42], although PCL and PLA are The thermodynamic entropy exhibits incompatible properties, but the resulting PCL-g-CNs show good dispersibility in PLA, thus greatly improving the mechanical properties of the composite. Goffin et al. [43] also used a "grafting" method to graft a PLA molecular chain directly on the surface of the CNs by ring-opening polymerization (as shown in Figure 5), and then redisperse it into the PLA by twin-screw melt extrusion technology. The PLA chain grafted on the surface of the CNs not only enhances the compatibility of the CNs with the PLA matrix, but also co-crystallizes with the PLA matrix to form a co-continuous network. The mechanical properties of the final PLA-based nanocomposite are improved.

**Figure 7.** Polarized optical microscope images of PLLA, PLLA–CNC-1, and PLLA–SCNC-1 acquired on the 0, 5th and 10th min at 125 °C after quenched from melt at 210 °C. Scale bar, 200 μm. [38]
Figure 8. Grafting from method based on ROP of LA carried out via hydroxyl functionalities present at the CNs surface. [44]

3. Conclusion

The development of bio-based polymers is closely related to consumer and industrial needs. In this regard, PLA, as a member of bio-based polymers, is one of the most popular and promising “green” environmentally friendly materials in the application of food packaging, medical equipment, electrical and electronic equipment, and mechanical and automotive components. At the same time, however, PLA must be enhanced in terms of heat resistance, heat distortion temperature, crystallization rate, and impact resistance. As shown in this review, the preparation of PLA-based nanocomposites by the addition of nanocellulose is one of the effective methods for improving the properties of PLA. Nanocellulose is easily added to the PLA matrix by appropriate pre-dispersion, pre-mixing, masterbatch, surface treatment and grafting methods. For future research, although the dispersion of nanoparticles in PLA matrix is still a challenging problem in the preparation of high performance composites, it is interesting to note from the recent trends that the development of synergistic combinations of multiple fillers will be the basis for the preparation of high performance composites in the future. This will be an effective ways to greatly improve the overall performance of nanocomposites.

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