Eco-friendly and practical plastic food-packaging alternatives of all-biomass-derived nanocomposite films

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Article

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Abstract

Approximately 60% of plastic pollution originates from the food and beverage packaging. Complete degradation of the bio-based plastic packaging presently available, relies on garbage sorting, recycling, and composting. Herein, we showcase that naturally-degradable bioplastics as food packaging alternatives can be accomplished with all-biomass nanocomposite encompassing pullulan, nanocellulose (NC) and/or hydrophobic lignin (HBL) using simple approaches. NC and HBL were derived from corn stalk using a recyclable eco-friendly deep eutectic solvent (DES). Optimal dispersion of NC in pullulan through high-pressure homogenization produced a pullulan-NC (PNC) bio-nanocomposite film with mechanical strength enhanced to 76.6 ± 1.9 MPa. Single PNC film could serve as food inner-packaging; while it collaborated with kraft paper wrapping to compensate its inadequate water resistance, performing as packaging for dry powders, biscuits, and oil. Remarkably, a sandwich-like film, created by hot-pressing two outer layers of HBL-NC (LNC) films and one PNC film layer, exhibited desirable mechanical strength and water resistance. Varying the number of LNC and PNC layers achieved diverse composite films as food outer-packaging, including preserving and shopping bags, disposable cups and straws. Significantly, all these films are biosafe and readily degraded in nature without counting on composting or recycling, underlining their prospects in future industrialization and sustainability.

Introduction

Since the 1950s, plastics have been widely produced and utilized all over the world given their significant utility in human activities. To date, over 8.3 billion tonnes (Gt) of plastics have been refined from fossil fuels. However, the immense difficulty in degrading plastics has led to their accumulation as persistent pollutants, posing a severe crisis to both the environment and human health. In 2015, approximately 6.3 Gt of plastic waste was generated, and this figure is projected to reach 12 Gt by 2050. Regrettably, only about 21% of plastic waste has been recycled or incinerated, with the remainder being dumped into natural ecosystems. While significant scientific advancements have been achieved in the near-complete depolymerization of polyester plastics using enzymes as well as the development of biodegradable alternatives such as dimethylglyoxylate, renewable polycarbonates, and polyester materials, further time and effort are required to implement these solutions on a large scale. Consequently, concerns regarding plastic pollution have prompted numerous nations to enact new regulations and laws prohibiting the use of conventional fossil-based plastics. Additionally, they are advocating for the mandatory adoption of renewable plastics and actively supporting the research and development of alternative options, particularly biodegradable plastics.

Packaging is the largest market segment for plastics, constituting over 30% of global plastic consumption. Packaging materials, in general, require excellent barrier properties against water vapor and oxygen as well as strong mechanical strength and transparency. Over the past two decades, polylactic acid (PLA) and polyhydroxyalkanoates (PHA) have emerged as the most extensively researched biodegradable bioplastics for replacing fossil-based plastics in many fields including food
packaging. Commercial PHA-based plastic products, such as Biopol, have been available,[10] and progress has been made in producing PHAs through the use of reprogrammed microorganisms.[11] However, large-scale industrialization and application of PHAs in bioplastics still present challenges due to high production costs, material composition and molecular weight instability, and inadequate thermal and mechanical properties.[12–13] PLA-based composite packages have gained widespread market acceptance as temporary substitutes for traditional plastics, with a growing demand.[10] Nevertheless, the production of PLA-based plastics is energy-intensive, and they exhibit weak mechanical strength, slow degradation, and low chemical recyclablility, which raise concerns about their long-term viability.[9,14–15]

Notably, approximately 60% of plastic packaging is used in the food and beverage industry.[3] Developing alternative materials for fossil-based plastic food packaging would significantly contribute to mitigating the hazards posed by plastic waste. However, PLAs and PHAs currently account for only 1% of annual plastic production,[16] while food-packaging materials predominantly rely on polyethylene (PE), polypropylene (PP), polysters, and aluminum plastics. Consequently, efforts have been dedicated to the development of novel bioplastics exclusively derived from biomass to create high-strength food-packaging materials.[17] Several factors need to be considered, particularly for food-packaging materials, such as user- and eco-friendliness, prevention of gas generation, moisture and aroma permeation, property stability, and long-term protection against microbial contamination.[18–19] However, research on biomass-derived bioplastics has not fully addressed their potential applications in food packaging. Only few recent studies have demonstrated the primary use of bioplastics as straws,[17,20] whereas others are far from realistic applications owing to the complexity of the techniques, such as DNA-based bioplastic fabrication, which hinders scalability.[21]

In recent years, polysaccharides such as cellulose have emerged as sustainable biopolymers,[22] offering potential for the development of bioplastics[2] and novel packaging materials.[17, 19] Among these polysaccharides, pullulan stands out as a promising candidate for food packaging owing to its desirable attributes, including considerable mechanical strength, film-forming ability, good oxygen barrier properties, biodegradability, biocompatibility, antimicrobial capability,[23] and heat-sealing ability.[24] However, pullulan has certain limitations: (i) pure pullulan film or coating lacks sufficient mechanical strength to serve as a standalone packaging material,[23] and (ii) its superhydrophilicity makes it moisture-sensitive, leading to potential impairments in its mechanical and barrier properties due to water absorption or desorption.[25–26] Currently, extensive attention is being directed toward the utilization of nanofillers to enhance the mechanical properties, moisture resistance, and gas impermeability of polymeric materials through composite formation.[27] In this regard, nanocellulose (NC) emerges as an ideal candidate,[27–28] since it originates from cellulose, one of the most abundant materials on Earth. This underscores the potential scalability of NC for the development of new bio-based food-packaging materials.[27] Furthermore, it has been demonstrated that use of lignin, which coexists synergistically with cellulose in plants, can further enhance the water and moisture stability of cellulose and other polysaccharide-based composite films.[20,29–31] This presents an opportunity to explore lignin as an additional component for the creation of water-resistant bio-based food-packaging materials. Importantly,
the use of deep eutectic solvents (DESs) in the preparation of NC and lignin deserves attention, as DESs are now regarded highly cost-effective and environmentally friendly for biomass processing.\[28\]

In this study, we therefore explored practical engineering approaches to develop pullulan-based composite food-packaging materials. Initially, NC and hydrophobic lignin (HBL) were derived from corn stalks (CS) treated with DES. The obtained NC was utilized to create a composite film, namely pullulan-NC (PNC) composite film (Fig. 1). The mechanical properties of the PNC film were evaluated, along with its performance as an inner packaging material for food. Subsequently, the prepared HBL was employed to fabricate an HBL-NC composite film (LNC). A sandwich-like composite film, LNC-PNC-LNC, was then produced using a simple hot-pressing method (Fig. 1). The water resistance of this composite film was examined, and its suitability as an outer packaging material was assessed to determine its competitiveness against fossil-based and bio-based plastics available in the market. This study presents an easily implemented and scalable technique for the production of next-generation bioplastics derived entirely from biomass. These bioplastics hold great potential for safe and sustainable food-packaging applications.

**Results and Discussion**

**2.1. Eco-Friendly Preparation of NC and HBL from CS**

CS represent a significant agricultural waste in both China and the United States.\[32–33\] However, they contain abundant carbohydrates such as cellulose, hemicellulose, and lignin, which can be converted into functional materials.\[33\] In this study, CS was chosen as the source material for producing NC and HBL. Notably, instead of employing traditional alkali treatments\[32\] or TEMPO\[34\] treatments, a potentially environmentally friendly DES, glycine-lactic acid (DES\(_{LG}\)), was utilized to process the CS powder. The resulting insoluble solid was collected and further processed to obtain NC, whereas the remaining DES\(_{LG}\) solution was used to prepare HBL and recover the DES\(_{LG}\).

After treating the insoluble solid with a bleaching solution, the resulting powder was analyzed using Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and solid-state \(^{13}\)C nuclear magnetic resonance (SS \(^{13}\)C-NMR). The FT-IR spectra (Fig. 2a) indicated the disappearance of the characteristic peak at 1,520 cm\(^{-1}\), which corresponds to the C = C stretching vibration of lignin.\[35\] Instead, characteristic peaks at 1,050 cm\(^{-1}\) and 837 cm\(^{-1}\) emerged, indicating C-O stretching and glycosidic linkage vibrations between the d-glucose units of cellulose.\[36\] These findings confirmed that the powder consisted of cellulose isolated from CS (CSC). Additionally, a new peak at 1,730 cm\(^{-1}\) in the FT-IR spectra (Fig. 2a), attributed to C = O stretching vibration,\[37–38\] suggested that the CSC underwent modification involving lactate acid or glycine during DES\(_{LG}\) processing. XPS survey of CSC (Fig. 2b and c) revealed a peak at 288.3 eV assigned to C = O, whereas no N was detected in the XPS spectra,\[39\] indicating that CSC was modified solely by lactic acid. To further elucidate the chemical structure of the prepared CSC and confirm the presence of ester or ether bonds between cellulose and lactic acid, SS \(^{13}\)C-
NMR analysis was employed. The obtained spectra displayed a chemical shift at $\delta_C 173.8$ ppm, corresponding to C = O, and another peak at $\delta_C 20.5$ ppm, representing a methyl group, respectively (Fig. 2d and e). The SS $^{13}$C-NMR results confirmed that CSC was indiscriminately modified by lactic acid through both ester and ether bonds. Next, transmission electron microscopy (TEM) was employed to observe the CSC suspension. TEM images revealed the presence of nanofiber-like cellulose in the suspension, with an average aspect ratio of 112.0 ± 52.0 (Fig. 2f). These aspect ratios were larger than those of cellulose nanocrystals (CNCs) but smaller than those of cellulose nanofibrils (CNFs). Therefore, the name "NC" was assigned to them. Additionally, the aspect ratio of NC obtained through DES$_{LG}$ pretreatment was significantly higher than that obtained through sulfuric acid hydrolysis for 30 min (61 ± 24) (Figure S1a). This can be attributed to the mild reaction conditions in DES$_{LG}$ pretreatment and the inhibitory effect of non-cellulosic components in CS on cellulose hydrolysis during the DES$_{LG}$ processing. In contrast, sulfuric acid is too strong and can hydrolyze both the amorphous and crystalline regions of cellulose. Furthermore, the NC obtained through DES$_{LG}$ processing showed excellent dispersion in distilled water with a polydispersity index of 0.7, and the NC suspension remained stable without aggregation for up to 3 months. This is likely due to the presence of lactate moieties on NC, which introduce negative charges that repel each other, as indicated by the zeta potential of -24 mV for the NC suspension.

Meanwhile, water was used to precipitate the dissolved substance in the DES$_{LG}$ solution. The resulting brownish powder (Fig. 2g) was analyzed using 2D-HSQC NMR and FT-IR. The 2D-HSQC NMR spectroscopic analysis revealed that the chemical constituents of the obtained powder consisted of Syringa (S) ($S_2, S_6, \delta_C/\delta_H 103.5/6.70$), Guaiac (G) ($G_2, \delta_C/\delta_H 110.4/6.99; G_5, \delta_C/\delta_H 116.2/6.78; G_6, \delta_C/\delta_H 119.5/6.79$), $p$-coumaric acid ($PCA, \delta_C/\delta_H 130.1/7.46$), $p$-benzoate ($PB, \delta_C/\delta_H 131.6/7.77$), and $p$-hydroxycinnamyl alcohol terminal groups ($l, \delta_C/\delta_H 66.2/4.20$), which are characteristic units of lignin. Furthermore, these units were primarily interconnected by $\beta$-O-4' aryl ether linkages ($Aa, \delta_C/\delta_H 72.4/4.92; A\beta, \delta_C/\delta_H 83.8/4.39$ and $A\gamma, \delta_C/\delta_H 60.2/3.50$) and $C\beta-C\beta'$ bonds ($Ba, \delta_C/\delta_H 83.8/4.97$ and $By, \delta_C/\delta_H 71.2/3.81$), forming a three-dimensional structure (Fig. 2h-i and S1c). Similarly, the FT-IR spectrum of the powder showed characteristic peaks associated with lignin (Figure S1b). Collectively, these analyses confirmed that the brownish powder constituted natural lignin and demonstrated the successful preparation of HBL.

Notably, the preparation process of NC and HBL from CS was established on a pilot scale, with yields of 22.1 ± 0.5% and 13.7 ± 0.6%, respectively (Table S1). The total biomass utilization of CS reached 35.8%, significantly higher than that of CS treated with alkali (26.4%). Furthermore, the DES$_{LG}$ could be recycled by evaporating water under a vacuum atmosphere, with a recovery rate of 73.1% (Table S1). The recovered DES$_{LG}$ could be reused four more times for processing CS, with consistent performance.
achieved by replenishing the lactic acid to its initial weight to compensate for the loss caused by cellulose modifications (Table S1). This demonstrated the favorable recyclability of DES_{LG}. Additionally, the processing of CS using DES_{LG} (four times) imposed a low environmental burden, as indicated by an E-factor of 27.3. These characteristics highlight the eco-friendly advantages of this technique and suggest its potential for industrialization. While, further endeavors should be devoted to the recovery of the residuals in the used DES_{LG}, probably hemicellulose, and develop their utilizations, hoping to achieve full recycling of CS.

2.2. PNC Nanocomposite Film

The obtained NC was employed as an enhancer to improve the mechanical properties of pullulan films. As a result, the addition of NC increased the tensile strength (TS) of the PNC film from 43.7 ± 2.6 MPa to 76.6 ± 1.9 MPa as the NC content increased from 0 mg/g pullulan to 25 mg/g pullulan (Fig. 3a). However, a notable decrease in TS was observed when the NC content reached 30 mg/g pullulan (Fig. 3a). Furthermore, the elongation at break (EB) decreased significantly from 12.2 ± 0.3% to 4.7 ± 0.2% with an increasing NC content of 0 mg/g pullulan to 30 mg/g pullulan (Fig. 3a). PNC_{20} and PNC_{25} films exhibited considerably higher TS (approximately 75.6 MPa) than other natural polymeric materials such as DNA-based bio-plastic and poly(epichlorohydrin-co-ethyleneoxide)-based ionomers (1 MPa),\textsuperscript{[49]} chitosan-cellulose nanofiber-hemicellulose composite films (38.6 MPa),\textsuperscript{[50]} and soybean protein nanostructured films (15.6 MPa).\textsuperscript{[51]} Moreover, the TS of PNC_{20} and PNC_{25} films outperformed that of conventional fossil-based packaging plastics such as polystyrene (PS) (30.0–35.0 MPa), polypropylene (PP) (25.0–40.0 MPa), polyethylene terephthalate (PET) (75.0 MPa), and low-density polyethylene (LDPE) (15.0 MPa)\textsuperscript{[52]} as well as recyclable synthetic materials, including poly(\(\gamma\)-butyrolactone) (PyBL) and poly(trans-hexahydrophthalide) (PT6HP) (7.4–28.8 MPa),\textsuperscript{[9]} and bio-based plastics like poly-hydroxyalkanoates (PHAs) (40.0 MPa) and PLA-poly(butyleneadipate-co-terephthalate) (PBAT) composites (65.0 MPa)\textsuperscript{[53]} (Fig. 3b). Additionally, the EB values (approximately 7.3%) of PNC_{20} and PNC_{25} films were significantly lower than those of the aforementioned materials (Fig. 3b and Table S2). While the reduced EB may limit the use of PNC films as tensile packaging plastics like cling films, it can prevent PNC-based packaging from excessive stretching when used for PLA-based packaging plastics and lifting of heavy objects. Moreover, the TS and EB of PNC_{20} and PNC_{25} films showed no significant differences across varying thicknesses (0.03 mm to 0.13 mm) (Table S3). The maximum force at break (MF) for the thinnest PNC_{20} film (thickness: 0.03 mm) was 35.4 N, whereas that for the 0.03 mm-thick PLA-PBAT film was 2.5 N (Table S3). As a result, a 0.03 mm-thick PNC_{20} film belt (length: 8 cm; width: 0.5 cm) could easily lift 1 kg of weight without being fractured or noticeably stretched (Figure S2a). Overall, these results indicate that the mechanical performance of pullulan films can be significantly enhanced by incorporating pullulan-NC composites. PNC nanocomposite thin films demonstrate mechanical properties competitive with those of other plastic/bioplastic materials currently in practical use or under investigation. This development meets the fundamental requirement for their potential application as alternative materials for food packaging.
Importantly, no significant differences were observed in the TS and EB between the PNC$_{20}$ and PNC$_{25}$ films, highlighting the need to confirm the ideal film formulation. Additionally, the substantial enhancements in the mechanical properties of the PNC films prompted us to identify a general principle for enhancing the mechanical strength of other polysaccharide-based materials. To achieve this objective, the distribution of NC within the PNC films was initially investigated using X-ray diffraction (XRD) patterns, atomic force microscopy (AFM), and polarized light microscopy (POM). The XRD patterns revealed a single broad diffraction peak at 19° in the spectra of the PNC$_{5}$-PNC$_{20}$ films, indicating the presence of amorphous pullulan.$^{[54]}$ However, this peak split into two peaks at 19° and 22.6° for the PNC$_{25}$ and PNC$_{30}$ films, respectively (Fig. 3c). The appearance of the 22.6° peak suggested the occurrence of crystalline-state NC$^{[55]}$ and the phase separation of NC from the pullulan matrix. Furthermore, AFM and POM observations of the PNC films demonstrated that the surfaces of the PNC$_{20}$ films were highly smooth without any noticeable aggregates. In contrast, the surface of the PNC$_{25}$ film exhibited slight roughness with the formation of small aggregates, whereas the PNC$_{30}$ films displayed obvious roughness with visible aggregates (Fig. 3d-f and S2b). This can be attributed to the gradual aggregation of NC within the pullulan matrix as the concentration increased. Consequently, NC was uniformly dispersed in the PNC$_{5}$-PNC$_{20}$ films, whereas aggregation began to occur in the PNC$_{25}$ film. However, this aggregation became significant in the PNC$_{30}$ film, which likely contributed to its substantial decrease in mechanical strength. Overall, based on the findings, the optimal film formulation was determined to be PNC$_{20}$. The improved dispersion of NC within the pullulan matrix in the PNC$_{20}$ film likely resulted in stronger internal interactions,$^{[56]}$ as subsequently confirmed by the following assays.

As observed in the preceding analysis, modification of NC with lactic acid, which has received limited attention in previous studies, was conducted in this study. The disparate dispersions of NC in the PNC$_{20}$ and PNC$_{30}$ films (Fig. 3d-f and S2b) may give rise to diverse intermolecular interactions. Subsequently, the internal interactions within the PNC films were examined by investigating the rheological behavior of the pullulan-NC composite solution (PNS) and conducting FT-IR analyses of the PNC films. The rheological behavior of the PNS revealed that the intermolecular interactions were strengthened by the incorporation of NC into PNS, reaching a maximum effect at an NC content of 20 mg/g pullulan (Figure S3). Moreover, the FT-IR spectra of the PNC films displayed peak shifts in the hydrogen group region, ranging from 3,000 cm$^{-1}$ to 3,700 cm$^{-1}$,$^{[57]}$ when compared with those of the single pullulan film. This finding indicated the formation of hydrogen bonds in the tested PNC films (Fig. 3g-i and Table S4). Notably, the fraction of hydrogen bonds ($F_{H-OH}$) in the PNC films progressively increased with the increasing NC content, reaching a peak value of 0.742 ± 0.008 in the PNC$_{20}$ film (Fig. 3i). These results suggested that the formation of additional intermolecular hydrogen bonds played a vital role in enhancing the mechanical properties of pullulan through the inclusion of a nanofiller such as NC.

Furthermore, the higher $F_{H-OH}$ observed in the PNC$_{20}$ film compared with those in the PNC$_{30}$ films corresponded to its more homogeneous dispersion within the pullulan-NC composites (Fig. 3d-f and S2b). This observation indicated that the well-dispersed NC facilitated the formation of a greater number of
intermolecular hydrogen bonds. In contrast, the acetylation of hydroxyl groups in NC (yielding acetyl-NC) led to a reduction in the TS of the pullulan-acetyl-NC (PANC) nanocomposite films (Figure S4). This finding demonstrated the significance of intermolecular hydrogen bond quantity in enhancing the mechanical strength of the pullulan-NC nanocomposite film. Therefore, the fundamental approach to enhance the mechanical properties of a film-forming polysaccharide is to employ a nanofiller capable of forming robust intermolecular hydrogen interactions with the polysaccharide, and simultaneously to achieve a homogeneous dispersion of the nanofiller within the polysaccharide matrix.

2.3. Food Packaging Material Consisting of Inner PNC Film and Outer Kraft Paper

Although the PNC\textsubscript{20} film showed sufficient mechanical strength, which would benefit the protection of the packaged contents against external forces during storage and transportation, it exhibited an unsatisfactory vapor barrier capability (water vapor permeability [WVP] = 0.032 ± 0.002 g·m·[m\textsuperscript{2}·d·kpa]\textsuperscript{-1}) compared with that of recycled chemical synthetic polymer film (Fig. 4a).\textsuperscript{[9]} Consequently, this film demonstrated intolerance to relative humidity (RH) exceeding 53% after prolonged exposure, leading to a significant decrease in mechanical strength as indicated by its TS (Fig. 4b). However, the PNC\textsubscript{20} film exhibited advantageous oxygen barrier capability (oxygen permeability; peroxide value [PV] = 49.4 ± 0.4 meq/kg) (Fig. 4a), folding endurance (Fig. 4c), heat sealability (heat sealing strength = 1.60 ± 0.08 kN/m) (Figure S5a), high transparency (Figure S5b), and non-toxicity (Figure S5c and d). Collectively, these properties indicate that the PNC\textsubscript{20} film is suitable for use as a food inner-packaging material, commonly used in food products with individual small packages such as Oreo cookies and Nescafé sticks. However, to prevent moisture ingress, it is necessary to use an outer packaging material to enclose the PNC\textsubscript{20} film.

In this study, kraft paper, the most conventional and readily available outer packaging material, was selected. When the PNC\textsubscript{20} film was sealed within a kraft paper wrap, its TS showed no significant deterioration under various humidity conditions for 7 days (Fig. 4b). This suggests that the combination of the PNC\textsubscript{20} film and kraft paper wrap may be suitable for use in food products with individual packages.

Next, to evaluate the performance of this food-packaging system, three different food items, namely soluble coffee powder, biscuits, and olive oil, were individually packed in heat-sealed PNC\textsubscript{20} bags and then wrapped with kraft paper (Fig. 4d). The preservation effects were assessed after storing the packed items at 53% RH for 12 months. Figure S6a-d illustrates that the quality of the food items wrapped in the PNC\textsubscript{20}/kraft paper packaging was comparable to that packed in PET bags (Figure S5e) in terms of moisture content for soluble coffee powder and biscuits and PV for olive oil and crisp biscuits. These results demonstrate that the PNC\textsubscript{20}/kraft paper packaging can effectively preserve these foods, extending their shelf life. Moreover, upon peeling off the kraft paper wrap, the individual PNC\textsubscript{20} bags were capable of maintaining the quality of the foods for up to 3 days without significant moisture adsorption or softening (Figure S6e-f). Additionally, the PNC\textsubscript{20} bag demonstrated rapid decomposition in hot water, fully
dissolving the coffee within 50 s of stirring (Figure S6g). Therefore, it can also serve as edible packaging for food products that require dispersion in hot water. This packaging combination, employing PNC_{20} as the inner-packaging material and kraft paper as the outer layer, presents a promising alternative for preserving instant drinks, convenient snack foods and oil flavors (Movie 1).

Importantly, after being buried in soil for only 10 days, the PNC_{20} bags underwent almost complete degradation, with no visible remnants (Fig. 4e), with a degradation rate of 83.4 ± 1.1% (Table S5). In contrast, under the same conditions, PLA and PBAT films retained their original shapes and showed an average degradation rate of only 1.1 ± 0.3%.\textsuperscript{[14, 58]} This finding is of great significance, as it indicates that the PNC_{20} inner packaging can undergo rapid degradation in the natural environment, thereby significantly reducing the additional environmental impact and labor required for waste sorting and recycling. Furthermore, kraft paper, which is naturally biodegradable, is an environment-friendly material. Overall, the PNC_{20} film introduced in this study holds promise as an alternative to conventional plastic food-packaging material.

### 2.4. Sandwich-Like Lignin-Pullulan-NC (LPLNC) Nanocomposite Film as Food Outer-Packaging Material

To address the inadequate water resistance of the PNC_{20} film and enable its use as a food outer packaging material, we utilized HBL (prepared as described in section 2.1) to create a sandwich film (LPLNC). The LPLNC film consisted of HBL-based films as the outermost layers and the PNC_{20} film as the middle layer (Fig. 5a), which were formed through hot pressing. However, notably, HBL alone cannot form films. Therefore, we mixed HBL with NC (initial lignin/NC weight ratio, L/C = 1:2) to fabricate an HBL-NC composite (LNC) film. The resulting LNC film had a thickness of 0.03 mm, which is the thinnest dimension that allows film formation. However, when two layers of this thickness of LNC and one layer of the PNC_{20} film were hot-pressed together, the resulting LPLNC film became highly brittle and prone to cracking upon folding. To address this issue, we initially adjusted the L/C ratio of the LNC composite film to 1:6 or 1:1, but it had no effect on the brittleness of the LPLNC film. Interestingly, we discovered that the brittleness of the LPLNC films (L/C = 1:2) decreased with an increase in glycerol content in the PNC_{20} film, while their TS showed a slight decrease. When the glycerol content reached 300 mg/g pullulan in the PNC_{20} film (referred to as PNC_{20}-G300 film), the resulting LPLNC-2 film exhibited the most balanced performance, with a TS of 36.7 ± 1.3 MPa and folding endurance 1,000 times in magnitude (Fig. 5b-d). Although the L/C ratio of the LNC film did not affect the brittleness of the LPLNC film, as mentioned earlier, it did influence the water resistance properties of the LPLNC-2 film. Specifically, an increase in the L/C ratio enhanced the water resistance of the LNC film. When the L/C ratio was 1:3 in the LNC-2 film, the resulting LPLNC-3 film demonstrated favorable water resistance properties (water absorption: 136.8 ± 11.7%; contact angle: 63.6 ± 2.3° in 350 s) and a TS of 35.1 ± 1.2 MPa (Fig. 5e-g). Thus, the LPLNC-3 film was identified as the optimal film and was fabricated using the PNC_{20}-G300 film (glycerol content: 300 mg/g pullulan) and the LNC-2 film with an L/C ratio of 1:3. The TS of the LPLNC-3 film was higher than
that of PLA-PBAT (8.5 MPa) (Figure S7a) and comparable to that of commercial polyolefin films such as PE and PP (20–40 MPa). However, its EB was significantly lower than that of biodegradable PLA-PBAT and commercial polyolefin films (Figure S7a). These mechanical properties indicate that the LPLNC-3 film can be utilized to develop high-strength food-packaging materials. However, further efforts are required to develop LPLNC-based thin films with extensibility, as the current version primarily serves as an elastic food-preserving thin-film wrap.

Different food-packaging materials require varying thicknesses for practical use. For instance, plastic bags used for food preservation and shopping generally have a thickness ranging from 0.05 to 0.07 mm, whereas plastic straws are approximately 0.4 mm thick, and disposable plastic cups are approximately 0.5 mm thick. The LPLNC-3 film mentioned earlier, with a thickness of 0.065 mm, fulfilled the requirements for making food-preserving shopping bags. This same LPLNC film was utilized for making straws and disposable cups. Initially, attempts were made to increase the thickness of the LNC-2 and PNC<sub>20</sub>-G300 films to 0.07 mm by layering them. However, during hot pressing, the PNC<sub>20</sub>-G300 film extruded from the interlayer of the two LNC-2 films. This indicated that the thickened film contained excessive material and could not be fully integrated with the outer layers. A new film, LPLNC-M, was therefore created by hot-pressing multiple layers of the LNC-2 and PNC<sub>20</sub>-G300 films. The layers were alternately overlaid on each other, with the LNC-2 film serving as the outermost layer on both sides (Fig. 5a). By adjusting the number of layers to 21 and 25, the thickness of the LPLNC-M films could be increased to 0.393 ± 0.003 mm and 0.508 ± 0.004 mm, respectively. Importantly, the TS values of these films were not significantly different from that of the LPLNC-3 film (three layers) (Table S6).

Based on the progress made, LPLNC-M films with various thicknesses were developed for applications in making food-preserving shopping bags (three layers), disposable cups (21 layers), and straws (25 layers) (Fig. 6a-d). The performance of these films was investigated, yielding the following findings. First, a preserving bag made of LPLNC-M successfully stored fresh beef at -20°C for 2 months without becoming brittle or sustaining damage from freezing (Fig. 6a and Figure S7b), and this LPLNC-M bag could be stored at 25°C and 53% RH for 12 months without significant change in mechanical strength (Figure S7c). Second, an LPLNC-M shopping bag demonstrated its high strength by easily supporting a weight of 700 g without deformation or breakage (Fig. 6b). Third, an LPLNC-M cup exhibited the ability to hold water overnight without leaking (Fig. 6c), even when initially filled with boiling water. However, despite multiple layers being hot-pressed, molding LPLNC-M films into bottles proved challenging. This hurdle may be attributed to the insufficient rigidity of the LPLNC-M films, which warrants further investigation in future studies. Lastly, an LPLNC-M straw (Fig. 6d) successfully siphoned water, maintaining its shape without obvious deformation after being submerged for 1 h (Figure S7d). This demonstrates the potential of LPLNC-M films as a substitute for conventional plastic straws and degradable bioplastic straws, such as the Starbucks straw made of coffee grounds and PLA composites (Fig. 6d). All the performance can also be overviewed in Movie 2.
The LPLNC-M film-based food-packaging materials and expendables demonstrated performance comparable to that of commercial products in recent studies.\[51, 60-61\] These films exhibited easy biodegradability in natural environments, completely disintegrating after being buried in soil for 5 weeks (Fig. 6e). This biodegradability can be attributed to the components of the films, including pullulan, lignin, and cellulose. In contrast, commercial PLA-PBAT packages maintain their original shape when buried in soil for the same duration (Fig. 6e). However, they degrade after an additional 6 months of composting\[62\] and take hundreds of years to degrade in the oceans.\[58, 63\] The only minor drawback of the LPLNC-M film is its dark brown color, which hinders clear observation of the food and beverage inside the packages. Addressing this issue requires the development of advanced techniques to improve the transparency of the film using non-lignin biomass-based materials, which can also enhance water resistance.

Importantly, all the raw materials used for the food-packaging films in this study, including pullulan, NC, and lignin, were obtained from biofabrication processes. These processes involved yeast fermentation and recyclable biorefinery of agricultural stalk waste using DESs. Furthermore, the fabrication of these films involved physical methods such as high-pressure homogenization, drying, and heat pressing. These approaches are much simpler to implement than the chemical processing of wood chips and maize cobs with aldehydes, necessary to convert these inedible biological materials into biodegradable polyesters like dimethylglyoxylate xylose.\[16\] Consequently, the techniques employed in this study for fully biomass-based food packaging present novel strategies for the production of bioplastic materials with favorable eco-friendly characteristics. However, the sustainability of these materials is yet to be assessed, as bio-based plastics do not inherently offer sustainability superior to fossil-based plastics.\[2\] Additionally, concerns regarding their cost and energy efficiency must be resolved. Nevertheless, the bioplastic packages in this study exhibit rapid natural degradation, enabling them to easily enter Earth's natural carbon cycle at the end of their lifespan. As a result, they can be converted into carbon sources for fermentation and contribute to the production of stalks for NC and lignin, effectively closing the loop of matter cycling in bioplastic packaging, as demonstrated in this work. This eliminates the need for specialized composting, labor-intensive sorting, and recycling processes typically required for PLA-based plastics. Notably, in several underdeveloped countries, there may be insufficient resources to sort and recycle PLA-based plastics, making the rapid natural degradation of these new bioplastics an advantageous feature. Overall, our findings suggest that bioplastic packaging would have minimal end-of-life impact on the environment and the economy, indicating its potential as an alternative to fossil-based food packaging.

**Conclusion**

In this study, we demonstrated that by effectively utilizing biomass-derived raw materials such as pullulan, NC, and lignin, it is possible to develop bioplastic films that exhibit performance comparable to that of bio-based and fossil-based plastics in food packaging. Importantly, these bioplastics exhibit significant potential for practical applications. This can be attributed to the following reasons: (1) Pullulan, a readily available commodity with a long history of use, serves as the raw material, making it
easily accessible; (2) The biorefinery process for obtaining NC and HBL involves environment-friendly DES-assisted methods that utilize CS waste as sources; and (3) The fabrication of these films employs simple composite and practical physical approaches. Notably, the rapid biodegradation of these bioplastics in the natural environment suggests that they can easily integrate into ecosystems, potentially eliminating the need for recycling and composting at the end of their life cycle. This characteristic, combined with the advantages offered by the raw materials and fabrication techniques employed in the film production, aligns with the principles of green chemistry and sustainable development. Despite the introduced bioplastics currently fall short of fossil-based plastics in terms of economic feasibility and efficiency, they pave the way for the development of truly eco-friendly bioplastics capable of transitioning to a circular economy. Building upon these advancements, it is possible to develop all-biomass-derived general and engineered plastics by addressing the remaining challenges related to extensibility and rigidity.

Declarations

Supporting Information

Supporting Information is available online or from the author.

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References

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Figures

Figure 1

Schematic illustration depicting the architectural designs of bioplastic alternatives for food packaging in this study.
Figure 2

(a) FT-IR spectra of CS, DES$_{LG}$ treated-CS, and bleach treated-CS. (b) XPS total spectrum and high-resolution C1s spectrum (c) of CSC. (d) SS $^{13}$C NMR spectrum of CSC. (e) SS $^{13}$C-NMR curve-fitting spectra of CSC in the range of 168 ppm-181 ppm. (f) Transmission electron microscopy (TEM) images and histogram of the aspect ratio on the upper right corner of NC. Scale bar = 100 nm. (g) Photograph of the brownish powder extracted from the DES$_{LG}$ solution. (h-i) 2D-HSQC spectra of the brownish powder extracted from the DES$_{LG}$ solution.
Figure 3

(a) Tensile strength (TS) and elongation at break (EB) of pullulan film (PF) and PNC films (b) compared with those of previously reported materials: 1. DNA plastics; 2. soy protein isolate (SPI) film; 3. thermoplastic starch-nanocellulose composites; 4. pullulan-carboxylated cellulose nanocrystal composites; 5. hemicelluloses-chitosan-based edible films; 6. cellulose nanocrystals-cellulose nanofibril composites; 7. PHAs; 8. PLA; 9. PBAT; 10. PS; 11. PET; 12. LDPE; 13. PP; 14. PyBL-PT6HP composites;
and 15. PNC$_{20}$ and PNC$_{25}$ films in this study. Data are presented as mean ± SD (n = 3). Data with different superscript letters indicate significant differences. (c) X-ray diffraction (XRD) curves of PF and PNC films with various NC contents. (d-f) Atomic force microscopy (AFM) images of PNC$_{20}$, PNC$_{25}$, and PNC$_{30}$ films. (g) ATR-FTIR total spectra. (h) Hydroxyl stretching vibration region and its curve-fitting spectra of the PNC$_{20}$ film (upper right corner). (i) Hydrogen bonding fraction ($F_{\text{H-OH}}$) of the PF and PNC films. Data are presented as mean ± SD (n = 3). Data with different superscript letters indicate significant differences.

Figure 4

(a) Water vapor and oxygen barrier capabilities of the PNC$_{20}$ film and PLA&PBAT film. (b) Tensile strength (TS) values of PNC$_{20}$ film with and without kraft paper packaging, stored at 33%, 53%, and 83% relative humidity for 0 day, 3 days, and 7 days. (c) Ratios of TS values before and after repeated folding ($\delta/\delta_0$) of the PNC$_{20}$ film. Data are presented as mean ± SD (n = 3). Data with different superscript letters indicate significant differences. (d) Photographs of coffee, olive oil, and biscuits in individual PNC$_{20}$ inner packages and combined with kraft paper outer packages. (e) Appearance of PNC$_{20}$ and PLA&PBAT film after burial in soil for various durations. Scale bar = 1 cm.
Figure 5

(a) Schematic representation of the fabrication process for LPLNC films. (b) Tensile strength (TS) values and (c) folding endurance of LPLNC films with varying glycerol contents in the PNC\textsubscript{20} film. (d) Ratios of TS values after repeated folding compared with initial TS values ($\delta/\delta_0$) of the LPLNC film with a glycerol content of 300 mg/g pullulan in the PNC\textsubscript{20} film. (e) TS values and (f) water absorption of LPLNC films with different lignin/NC ratios (L/C) in lignin-NC nanocomposite (LNC) films. (g) Contact angle of LPLNC films with L/C ratios of 1:3 and 1:6 in the LNC film over a time range of 0 s to 360 s. Data are presented as mean ± SD (n = 3). Data with different superscript letters indicate significant differences.
Figure 6

(a) Photographs of the LPLNC-M food-preserving packaging material containing fresh beef before and after storage at -20 °C in a refrigerator for 2 months. (b) Photographs of the LPLNC-M shopping bag before and after lifting two bottles of coke. (c) Photograph of the LPLNC-M disposable cup made from film. (d) Photographs of the LPLNC-M straw; Starbucks straw made of PLA and coffee grounds; the process of sucking water through the LPLNC-M straw. (e) Photographs of the LPLN-M films (25 layers) and PLA-PBAT bags after being buried in soil for different durations.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.