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Preparation of Formyl Cellulose and Its Enhancement Effect on The Mechanical and Barrier Properties of Polylactic Acid Films

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Abstract: Cellulose was modified by formic acid to prepare formyl cellulose (FC). The amount of formyl groups in FC was adjusted by controlling the reaction time, reaction temperature, and formic acid concentration. Then, FC was used to reinforce polylactic acid (PLA) films prepared by solution casting. Scanning electron microscopy (SEM) shows that long rod-like cellulose particles were broken into short rods after formylation and the introduction of FC made PLA surface rougher. The mechanical properties of PLA/FC films

were improved by the inclusion of FC. Compared to pure PLA film, the PLA/FC composite film with 1 wt% FC (containing 15.79% formyl groups) showed a 48.59% increase in tensile strength and a 346% increase in Young's modulus. The addition of FC also resulted in better water barrier properties. The moisture absorption capacity and water vapor permeability were 40.56% and 51.43% lower than those of the pure-PLA film. The enhancement in properties for PLA/FC composites could be ascribed to the improved compatibility between PLA and cellulose with the introduction of hydrophobic formate group. The PLA/FC composite films developed in this work could be highly potential for food packaging.

Keywords: Polylactide; Formyl cellulose; Mechanical properties; Film barrier properties; Film transparency; Moisture absorption

1. Introduction

Nowadays, the wide application of petroleum-based synthetic plastics in food packaging has caused serious environmental issues [1-3]. The development of new polymer materials based on natural renewable resources has attracted considerable attention [4-6]. Among various biopolymers, polylactic acid (PLA) has been considered as one of the most promising biobased polymers for food packaging [7-9]. PLA is derived from natural and renewable resources such as corn, wheat, and sugarcane. It is relatively cheap, transparent, biodegradable, biocompatible, and easily processable. Therefore, efforts have been increasingly devoted to developing PLA-based packaging materials in recent years [10-12]. Packaging materials with improved barrier properties could increase the shelf-life of food products as they prevent the products from spoilage by maintaining the moisture and gas

conditions within the package for food. However, the mechanical and barrier properties of PLA are not as satisfactory as those of conventional petroleum-based plastics, which limits its application as a food packaging material [13,14].

To improve the mechanical and barrier properties of PLA-based packaging films, it is promising to use cellulose to reinforce PLA matrices. Cellulose is the most abundant polysaccharide in nature and is biodegradable and biocompatible. It has been widely reported that cellulose was modified or converted to micro- and nano-cellulose, and then blended with PLA to produce PLA/cellulose composites with improved performance [15-18]. For example, Xiao et al. [19] synthesized an L-lactic acid oligomer-grafted microcrystalline cellulose (g-MC) and blended it with PLA to fabricate PLA/g-MC films. The tensile strength of such composite films was about 50% higher than that of pure PLA. Qian et al. [20] reported that the inclusion of bamboo cellulose nanowhiskers (BCNW) into a PLA matrix resulted in increases in elongation at break and Young's modulus. The elongation at break of PLA films increased from 17.7% (without BCNW) to 22.27% (at 1.0 wt% loading) and the Young's modulus increased from 411.51 MPa (without BCNW) to 427.72 MPa (at 2.5 wt% loading). Sanchez-Garcia et al. [21] found that the addition of CNW effectively improved the barrier properties of PLA film. When the loading of CNW was 3 wt%, the reductions in water vapor permeability (WVP) and oxygen permeability were up to 82% and 90%, respectively.

Most manufacturing processes for micro- and nano-cellulose are not cost-effective enough or requires large amounts of chemical solvents [22,23]. Specifically, the mechanical processes used for this purpose such as high-pressure homogenization and ball-milling [24,25]

are energy-intensive. The chemical approaches using strong acids produce wastes that are difficult to be recovered after the reaction [26]. The biological processes involving enzymes and bacteria usually take a long time and the yields are usually low [27]. Green and economical ways to produce new types of modified cellulose are still highly demanded for developing PLA-based composites. In previous studies, our group demonstrated that formic acid pretreatment could increase cellulose accessibility by the fractionation of main lignocellulose components (cellulose, hemicellulose, and lignin) [28]. The formylation of cellulose occurred during the treatment. The obtained formyl cellulose (FC) is usually considered to be a valueless byproduct as it is harmful to the fermentation process to produce bioethanol. Nonetheless, hydrophobic groups introduced onto cellulose chains by formylation were found to improve the compatibility between cellulose and a polymer matrix [29]. Besides, the properties of FC may be adjusted by reaction conditions, which makes it possible to fabricate PLA/FC composites with tailored properties. Moreover, the formic acid used for the reaction can be easily recycled through a vacuum distillation process to minimize its environmental impact. To the best of our knowledge, the fabrication and properties of PLA/FC composites have not been reported.

In this study, cellulose was treated with formic acid to produce FC and the formylation degree of FC was tuned by reaction temperature, reaction time, and formic acid concentration. Then, the obtained FC was blended with PLA to prepare PLA/FC films by solution casting. The effects of FCs with different amounts of formyl groups on the morphology, structure, and properties of PLA films were investigated. The present work intends to develop

high-performance PLA/FC composite films useful for food packaging.

2. Materials and Methods

2.1 Materials and chemicals

Filter paper (98% of cellulose) was supplied by Hangzhou Special Paper Co., Ltd (China). Filter paper was chosen as the source of cellulose as it has a high content of cellulose (98%) so the impact of lignin and hemicellulose on the modification of cellulose can be minimized. PLA (Revode 190; $M_n = 9.7 \times 10^4$ g/mol, polydispersity index of 1.2, and L-lactate unit content of 98.5%, density of 1.25 g/cm³, $T_g = 55-60$ °, and $T_m = 170-180$ °C) was supplied by Zhejiang Hisun Biomaterials Co., Ltd (China). Formic acid (98% purity), sulfuric acid (98% purity), acetone (AR) and dichloromethane (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2 Preparation of formyl cellulose (FC)

Filter paper was cut into 10 mm × 10 mm rectangle shapes and then mixed with a formic acid solution at a solid-to-liquid ratio of 1:10 (g/mL) to obtain a suspension. Afterwards, the suspension was put into a three-neck round bottom flask and heated for reaction. The formic acid concentration (70–90 wt%), reaction temperature (70–90 °C), and reaction time (1–5 h) were adjusted to obtain FC with different content of formyl groups. After the reaction, the solid product was washed with distilled water to neutral, mixed with acetone, filtrated by a Buchner funnel, and then freeze-dried at -45 ° for 24 h to obtain the final product of FC. The yield of FC was calculated according to **equation (1)**:

$$\text{Yield} = \frac{\text{Weight of obtained FC}}{\text{Amount of cellulose in filter paper}} \times 100\% \quad (1)$$

2.3 Preparation of PLA/FC films

PLA/FC films were prepared according to the method of Reddy et al. [30] with modification. Specifically, 4.95 g of PLA powder and 50 mL of dichloromethane were mixed in a beaker and stirred at room temperature until complete dissolution. Meanwhile, 0.05 g of FC powder was mixed with 50 mL dichloromethane with sonication. Then, the FC suspension was mixed with the PLA suspension and stirred at room temperature until complete dispersion. The film-forming suspension was poured onto a glass petri dish and dried at room temperature for 12 h to obtain PLA/FC film. The FC content was 1 wt% for all PLA/FC composites prepared.

2.4 Determination of the amount of formyl group in FC

The amount of formyl group was determined according to the method of Sluiter et al. [31]. The measurement was conducted using a high-performance liquid chromatography (HPLC) system (LC-RID-10A, Shimadzu, Kyoto, Japan) equipped with an Agilent Hi-Plex H column and a RID-10A detector. The temperature of the Agilent Hi-Plex LC column was set to be 65 °C, the liquid phase was 0.005 mol/L of dilute sulfuric acid, and the flow rate was 0.6 mL/min.

2.5 Particle-size analysis of FC

The particle size analysis of FC was carried out by a laser diffraction particle analyzer (Rise-2028, Rise, Jinan, China). Sample solutions (2 wt %) were made by diluting cellulose with distilled water.

2.6 Scanning electron microscopy (SEM)

The morphologies of FC powder and PLA/FC composites films were observed with a scanning electron microscope (SU8010, Hitachi, Tokyo, Japan). Samples were fixed onto electrically conductive tape and then coated with gold. The magnification and accelerating voltage used were 2500× and 10 kV for FC and 5000× and 3 kV for PLA/FC composite films. Fractured PLA/FC samples were collected from tensile testing and the fractured surfaces were imaged.

2.7 Fourier-transform infrared (FTIR) spectroscopy

Fourier-transform infrared (FTIR) spectra for FC powder and PLA/FC composite films were obtained by an FTIR spectrometer (Nicolette Magna 550II, GMI, Ramsey, MN, USA). The measurement was performed over a wavenumber range of 4000–500 cm^{-1} at a resolution of 8 cm^{-1} .

2.8 X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis was performed using an X-ray diffraction system (X'Pert PRO, Malvern Panalytical, Almelo, Netherlands) over a 2θ range of 2–45° (for FC) or 3–60° (for PLA/FC composites) at a step size 0.02°. The radiation source was Cu K (wavelength $\lambda = 1.540 \text{ \AA}$) and the operation was at 40 kV and 15 mA. Crystallinity index (CI) was determined by **equation (2)** [28]:

$$CI = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (2)$$

where I_{002} is the peak intensity of the (0 0 2) lattice diffraction at $2\theta \approx 22.5^\circ$ for FC or 16.7° for PLA composite films, I_{am} is the peak intensity of the amorphous region at $2\theta \approx 18.7^\circ$ for FC and 19.6° for PLA composite films.

2.9 Tensile properties

Tensile testing was performed with a universal testing machine (JDL-5000N, Tianfa Instruments Co., Ltd, Yangzhou, China) at room temperature. The samples were conditioned for 24 h at room temperature before being cut into 40 mm × 20 mm rectangle strips and mounted in the grips for testing. The initial gauge length was 500 mm. The testing speed was 5 mm/min. The stress–strain curves were plotted to determine tensile stress (TS), elongation at break (EB) and Young’ modulus (YM) by the built-in software. For each sample, five specimens were tested and the average values of mechanical properties were calculated.

2.10 Light transmittance

The light transmittance of films was determined using a UV spectrophotometer (UV-2600, Shimadzu, Kyoto, Japan) according to the method of Lu et al. [32]. The wavelength range to calculate the light transmittance was 800 nm. The film samples were cut into 10 mm × 10 mm rectangle strips for the measurement. The light transmittance values were averaged from three repeats.

2.11 Moisture absorption (MA)

The moisture absorption (MA) of films were determined according to a method reported previously [33] with modification. The rectangle samples (10 cm²) were placed at 65% relative humidity (RH) until reaching a constant weight. Afterwards, the samples were submerged in water in a beaker to reach absorption equilibrium (which took about 24 h). The MA value was calculated using **equation (3)**:

$$MA = \frac{W_t - W_0}{W_0} \times 100 \quad (3)$$

where W_t and W_0 were the weights before and after being soaked in water for t h. The MA values were averaged from five repeats.

2.12 Water vapor permeability (WVP)

The WVP of films were determined according to a method reported previously [34] with modification. The rectangle samples (10 cm^2) were put into a sealed bottle, which were placed in an autoclave sterilizer (LDZX-30FBS, Shanghai Sher an Medical Instrument Factory, China) at a temperature of $120\text{ }^\circ\text{C}$ and a pressure of 110 kPa for 10 min. The samples before placing in the sterilizer and after 10 min of treatment and cooling to room temperature were weighed. The value of WVP was calculated by using **equation (4)**:

$$\text{WVP} = \frac{\Delta m}{t \cdot S \cdot P} \cdot e \quad (4)$$

where Δm is the change in film mass (kg) at time t (s), S is the area of film (m^2), e was the thickness of film (m), P was the saturated vapor pressure at $120\text{ }^\circ\text{C}$ (Pa). The WVP values were obtained by averaging from five repeats.

3. Results and discussion

3.1 Effects of reaction conditions on cellulose formylation

Table 1 shows that reaction time, reaction temperature, and formic acid concentration strongly influenced cellulose formylation. The amount of formyl group in FC increased with a longer reaction time. Besides, at the same reaction time and reaction temperature, higher formic acid concentration resulted in more formyl groups in FC. By using 90 wt% formic acid, 15.79% formyl groups could be formed in FC when formylation took place at $90\text{ }^\circ\text{C}$ for 5 h. However, it can be seen from **Table 2** that the yield of FC decreased with higher reaction

temperature, higher formic concentration, and longer reaction duration, possibly due to the degradation of polymer.

3.2 Morphology, particle size, and crystallinity of unmodified cellulose and FC

Figure 1 shows the SEM images of unmodified cellulose (filter paper) and FC.

Unmodified cellulose showed a long rod-like shape with a smooth surface. After formylation, cellulose particles were fragmented. Before formylation, the average particle size of cellulose was 346 μm while after formylation, it was 150 μm , as shown in **Figure 2**. The decrease in particle size means a higher specific surface and more exposed functional groups, which can improve the interaction between the modified cellulose and PLA. It is worth mentioning that in our preliminary experiment, we reduced the particle size of FC to 50 μm and used it as a filler for PLA. Inclusion of the 50 μm FC particles did not cause significant changes to PLA film properties compared to inclusion of the 150 μm FC particles. Further reducing the particle size would increase the cost dramatically. Therefore, 150 μm was chosen as the smallest filler size in the following study. Moreover, the CI of FC was slightly lower than that of unmodified cellulose, as shown in **Table 3**. In this regard, formylation might destroy hydrogen bonds and the crystalline structure in cellulose. Besides, for FC samples with a higher degree of formylation, the CI was higher. Likely, a greater extent of reaction also removed amorphous parts from the original cellulose.

3.3 Molecular interactions in unmodified cellulose and FC

Figure 3 shows that unmodified cellulose and FC samples with different amounts of formyl groups all had similar FTIR patterns. The broad band in the range of 3000–3700 cm^{-1}

is ascribed to the O—H stretching vibration of cellulose. The sharp band at 2901 cm^{-1} is ascribed to the C—H vibration [35]. The characteristic peak at 1630 cm^{-1} is due to the hydroxyl (—OH) bending of water molecules absorbed by cellulose [36]. The adsorption peaks at 1430 , 1368 , 1170 and 1050 cm^{-1} are characteristic of I_{β} cellulose [37].

Compared with unmodified cellulose, the curves for FC show a new characteristic peak at 1725 cm^{-1} , which is ascribed to the C=O vibration. The intensity of this peak increased with a higher degree of formylation. This result suggests the reaction between formic acid and cellulose hydroxyl groups to form ester groups [38].

3.4 Morphology of PLA and PLA/FC composite films

Figure 4 presents the SEM images of cross-sectional surfaces of PLA and PLA/FC composite films. The surface of the pure-PLA film was smooth. When the content of formyl groups was low, the dispersion of FC particles in PLA was poor due to their high hydrophilicity and poor compatibility with PLA. With the inclusion of FC, the surface of PLA became rough, which could be caused by the texture of FC.

3.5 Molecular interactions in PLA and PLA/FC composite films

Figure 5 shows the FTIR spectra for PLA and PLA/FC composite films. All films displayed very similar FTIR patterns, indicating no chemical reactions occurred between PLA and FC. The peak for C=O vibration at 1770 cm^{-1} moves to 1760 cm^{-1} , suggesting hydrogen bonding between the carbonyl group of PLA and the formyl group of FC. Similar changes in the FTIR spectrum was also found in another research by Haafiz et al. [39] where PLA was included with oil palm biomass microcrystalline cellulose to prepare composite films.

3.6 Crystalline structure of PLA and PLA/FC composite films

Figure 6 shows X-ray diffractograms for PLA and PLA/FC composite films. For all films, there were two peaks at $2\theta = 16.7^\circ$ and 19.6° related to the characteristic of the α -type crystalline structure. The inclusion of FC did not change the PLA crystalline structure significantly [40]. **Table 4** shows that the CI of composite films increased from 31.82% to 42.92% when the amount of formyl groups in FC increased from 0% to 15.79%. In this regard, hydrogen bonding between the formyl groups of FC and the carbonyl group of PLA matrix [41] might have assisted PLA crystallization.

3.7 Mechanical properties of PLA and PLA/FC composite films

Figure 7 shows that the inclusion of FC led to higher TS and YM but lower EB for PLA. With a higher degree of cellulose formylation, both TS and YM increased, whereas the changes in EB were moderate. The pure-PLA film had TS of 23.42 MPa, YM of 0.29 GPa, and EB of 8.3%. With 1 wt% loading of FC with 15.79% formyl groups, the TS and EB of PLA/FC composite films reached 34.80 MPa and 1.16 GPa, respectively, showing 48.59% and 346% enhancement, respectively compared to those of the pure-PLA film. This improvement is expected since FC became more hydrophobic when there are more formyl groups, which made it more compatible with PLA and more dispersed in the PLA matrix to form a network structure [42]. Furthermore, according to the XRD results, higher CI might also account for the better tensile properties. Meanwhile, strong interaction between FC and the PLA matrix and a higher CI could restrict PLA chain movement, leading to the reduced plasticity of composite films.

3.8 Light transmittance of PLA and PLA/FC composite films

Figure 8 shows the light transmittance data for PLA and PLA/FC composite films. The incorporation of FC containing more formyl groups resulted in reduced transparency for PLA films. For the PLA film included with FC with 15.79% formyl groups at 1 wt% loading, the light transmittance was 79.62%, a 10.86% reduction compared to that of the pure-PLA sample (89.33%). Likely, the dispersed cellulose particles in PLA blocked the transmission of light. Besides, the higher CI of PLA/FC composites with higher content of formyl groups favored the scattering of light and thus decreased the light transmittance [43]. It is worth mentioning that the transparency of PLA/FC composite films was higher than 70%, which can still be considered as transparent films for food packaging purposes [44].

3.9 Moisture absorption (MA) of PLA and PLA/FC composite films

Food packaging with low MA is favorable for food preservation. **Figure 9** shows that PLA/FC composite films had lower MA than the pure-PLA film. In this regard, the strong structure formed in the composite films limited water penetration, leading to reduced MA [45, 46]. Moreover, the MA of PLA decreased with a higher degree of cellulose formylation. In this regard, formylation of cellulose means the introduction of less hydrophilic formyl groups and the reduction of original hydroxyl groups which are highly hydrophilic. The MA value of the PLA/FC composite film with FC with 15.79% formyl groups at 1 wt% loading was 1.02%, a 51.43% reduction compared to that of the pure-PLA film (2.1%).

3.10 Water barrier properties of PLA and PLA/FC composite films

Figure 10 shows that with the addition of FC with higher content of formyl groups, the

WVP of PLA film became lower. The WVP value of the pure-PLA sample was 7.01×10^{-13} $\text{kg} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. PLA/FC composite films with formyl groups ranging from 1.86% to 15.79% had WVP of 6.56×10^{-13} , 6.12×10^{-13} , 5.70×10^{-13} , 4.86×10^{-13} , 4.42×10^{-13} , and 4.16×10^{-13} $\text{kg} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$, respectively. The PLA/FC film with 15.79% formyl groups at 1 wt% loading displayed a 40.56% reduction in WVP compared to that of the pure-PLA film. These results agree with the XRD analysis. More specifically, water molecules need more activation energy of diffusion to pass through composites films with higher CI and more compact structures [47]. Overall, the addition of FA, especially with higher content of formyl groups, effectively reduced WVP and improved water barrier properties for PLA films, which is beneficial for food preservation.

4. Conclusions

Cellulose was chemically modified by formic acid to produce FC, which showed significantly reduced particle size. The degree of cellulose formylation, as reflected by the amount of formyl groups introduced onto cellulose, was strongly affected by reaction time, reaction temperature, and formic acid concentration. In composites of PLA and FC, there was no chemical reaction between PLA and FC but there should be a greater degree of hydrogen bonding between the two, contributing to improved compatibility between them. The crystalline form of PLA was maintained with the addition of FC but a slight increase in CI was observed. The mechanical and barrier properties of PLA were effectively improved by FC addition. With inclusion of FC with 15.79% formyl groups at 1 wt% loading, the PLA composite film showed a 48.59% increase in TS and a 346% increase in YM, while the light

transmittance, moisture adsorption, and water vapor permeability were decreased by 10.86%, 51.43%, and 40.56%, respectively. Thus, this research demonstrates the effectiveness of FA, which can be prepared cost-effectively from original cellulose, to reinforce PLA. Also, the high potential of PLA/FC composite films in food packaging applications is shown.

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Declaration of interest

None

References

- [1] X.Z. Tang, P. Kumar, S. Alavi, K.N. Sandeep, Recent Advances in Biopolymers and Biopolymer-Based Nanocomposites for Food Packaging Materials. *Crit. Rev. Food Sci. Nutr.* 52 (2012) 426-442. [https://doi:10.1080/10408398.2010.500508](https://doi.org/10.1080/10408398.2010.500508).
- [2] J.W. Rhim, H.M. Park, C.S. Ha, Bio-nanocomposites for food packaging applications. *Prog. Polym. Sci.* 38 (2013) 1629-1652. [https://doi:10.1016/j.progpolymsci.2013.05.008](https://doi.org/10.1016/j.progpolymsci.2013.05.008).
- [3] N. Peelman, P. Ragaert, B. De Meulenaer, D. Adons, R. Peeters, L. Cardon, F. Van Impe, F. Devlieghere, Application of bioplastics for food packaging. *Trends. Food Sci. Technol.* 32 (2013) 128-141. [https://doi:10.1016/j.tifs.2013.06.003](https://doi.org/10.1016/j.tifs.2013.06.003).
- [4] M.G.A. Vieira, M.A. da Silva, L.O. dos Santos, M.M. Beppu, Natural-based plasticizers and biopolymer films: A review. *Eur. Polym. J.* 47 (2011) 254-263.

- <https://doi:10.1016/j.eurpolymj.2010.12.011>.
- [5] D. Briassoulis, A. Giannoulis, Evaluation of the functionality of bio-based food packaging films. *Polym. Test.* 69 (2018) 39-51.
<https://doi:10.1016/j.polymertesting.2018.05.003>.
- [6] F. Garavand, M. Rouhi, S.H. Razavi, I. Cacciotti, R. Mohammadi, Improving the integrity of natural biopolymer films used in food packaging by crosslinking approach: A review. *Int. J. Biol. Macromol.* 104 (2017) 687-707.
<https://doi:10.1016/j.ijbiomac.2017.06.093>.
- [7] I. Armentano, N. Bitinis, E. Fortunati, S. Mattioli, N. Rescignano, R. Verdejo, M.A. Lopez-Manchado, J.M. Kenny, Multifunctional nanostructured PLA materials for packaging and tissue engineering. *Prog. Polym. Sci.* 38 (2013) 1720-1747.
<https://doi:10.1016/j.progpolymsci.2013.05.010>.
- [8] C. Villegas, M.P. Arrieta, A. Rojas, A. Torres, S. Faba, M.J. Toledo, M.A. Gutierrez, E. Zavalla, J. Romero, M.J. Galotto, X. Valenzuela, PLA/organoclay bionanocomposites impregnated with thymol and cinnamaldehyde by supercritical impregnation for active and sustainable food packaging. *Compos. Part B Eng.* 176 (2019) 107336. <https://doi:10.1016/j.compositesb.2019.107336>.
- [9] M. Ghazali, S. Fahmiati, E. Triwulandari, W.K. Restu, D. Farhan, M. Wulansari, W. Fatriasari, PLA/metal oxide biocomposites for antimicrobial packaging application. *Polym. Technol. Mater.* 59 (2020) 1332-1342.
<https://doi:10.1080/25740881.2020.1738475>.

- [10] H. Moustafa, N. El Kissi, A.I. Abou-Kandil, M.S. Abdel-Aziz, A. Dufresne, PLA/PBAT Bionanocomposites with Antimicrobial Natural Rosin for Green Packaging. *ACS Appl. Mater. Interfaces*. 9 (2017) 20132-20141. <https://doi:10.1021/acsami.7b05557>.
- [11] F.L. Jin, R.R. Hu, S.J. Park, Improvement of thermal behaviors of biodegradable poly(lactic acid) polymer: A review. *Compos. Part B Eng.* 164 (2019) 287-296. <https://doi:10.1016/j.compositesb.2018.10.078>.
- [12] N. Mohamad, M.M. Mazlan, I.S.M.A. Tawakkal, R.A. Talib, L.K. Kian, H. Fouad, M. Jawaid, Development of active agents filled polylactic acid films for food packaging application. *Int. J. Biol. Macromol.* 163 (2020) 1451-1457. <https://doi:10.1016/j.ijbiomac.2020.07.209>.
- [13] J.W. Rhim, S.I. Hong, C.S. Ha, Tensile, water vapor barrier and antimicrobial properties of PLA/nanoclay composite films. *LWT - Food Sci. Technol.* 42 (2009) 612-617. <https://doi:10.1016/j.lwt.2008.02.015>.
- [14] A.J. Svagan, A. Åkesson, M. Cárdenas, S. Bulut, J.C. Knudsen, J. Risbo, D. Plackett, Transparent Films Based on PLA and Montmorillonite with Tunable Oxygen Barrier Properties. *Biomacromolecules*. 13 (2012) 397-405. <https://doi:10.1021/bm201438m>.
- [15] W. Yang, E. Fortunati, F. Dominici, G. Giovanale, A. Mazzaglia, G.M. Balestra, J.M. Kenny, D. Puglia, Effect of cellulose and lignin on disintegration, antimicrobial and antioxidant properties of PLA active films. *Int. J. Biol. Macromol.* 89 (2016) 360-368. <https://doi:10.1016/j.ijbiomac.2016.04.068>.

- [16] I. Gan, W.S. Chow, Antimicrobial poly(lactic acid)/cellulose bionanocomposite for food packaging application: A review. *Food Packag. Shelf Life*. 17 (2018) 150-161. <https://doi.org/10.1016/j.fpsl.2018.06.012>.
- [17] N. Hegyesi, Y. Zhang, A. Kohári, P. Polyák, X. Sui, B. Pukánszky, Enzymatic degradation of PLA/cellulose nanocrystal composites. *Ind. Crops Prod.* 141 (2019) 111799. <https://doi.org/10.1016/j.indcrop.2019.111799>.
- [18] E. Vatansever, D. Arslan, M. Nofar, Polylactide cellulose-based nanocomposites. *Int. J. Biol. Macromol.* 137 (2019) 912-938. <https://doi.org/10.1016/j.ijbiomac.2019.06.205>.
- [19] L. Xiao, Y. Mai, F. He, L. Yu, L. Zhang, H. Tang, G. Yang, Bio-based green composites with high performance from poly(lactic acid) and surface-modified microcrystalline cellulose. *J. Mater. Chem.* 22 (2012) 15732-15739. <https://doi.org/10.1039/c2jm32375g>.
- [20] S. Qian, H. Zhang, W. Yao, K. Sheng, Effects of bamboo cellulose nanowhisker content on the morphology, crystallization, mechanical, and thermal properties of PLA matrix biocomposites. *Compos. Part B Eng.* 133 (2018) 203-209. <https://doi.org/10.1016/j.compositesb.2017.09.040>.
- [21] M.D. Sanchez-Garcia, J.M. Lagaron, On the use of plant cellulose nanowhiskers to enhance the barrier properties of polylactic acid. *Cellulose*. 17 (2010) 987-1004. <https://doi.org/10.1007/s10570-010-9430-x>.
- [22] J.P. Siregar, J. Jaafar, T. Cionita, C.C. Jie, D. Bachtiar, M.R.M. Rejab, Y.P. Asmara, The Effect of Maleic Anhydride Polyethylene on Mechanical Properties of Pineapple

- Leaf Fibre Reinforced Polylactic Acid Composites. *Int. J. Precis. Eng. Manuf. Technol.* 6 (2019) 101-112. <https://doi.org/10.1007/s40684-019-00018-3>.
- [23] Z. Wang, Z. Yao, J. Zhou, M. He, Q. Jiang, A. Li, S. Li, M. Liu, S. Luo, D. Zhang, Improvement of polylactic acid film properties through the addition of cellulose nanocrystals isolated from waste cotton cloth. *Int. J. Biol. Macromol.* 129 (2019) 878-886. <http://doi.org/10.1016/j.ijbiomac.2019.02.021>.
- [24] S.Y. Lee, S.J. Chun, I. A. Kang, J. Y. Park, Preparation of cellulose nanofibrils by high-pressure homogenizer and cellulose-based composite films. *J Ind Eng Chem* 15 (2009) 50–55. [doi:10.1016/j.jiec.2008.07.008](https://doi.org/10.1016/j.jiec.2008.07.008).
- [25] S. Deng, R. Huang, M. Zhou, F. Chen, Q. Yu, Hydrophobic cellulose films with excellent strength and toughness via ball milling activated acylation of microfibrillated cellulose. *Carbohydr Polym* 154 (2016) 129–138. [doi:10.1016/j.carbpol.2016.07.101](https://doi.org/10.1016/j.carbpol.2016.07.101)
- [26] T. Zhao, Z. Chen, X. Lin, Z. Ren, B. Li, Y. Zhang, Preparation and characterization of microcrystalline cellulose (MCC) from tea waste. *Carbohydr Polym* 184(2018) 164–70. [doi:10.1016/j.carbpol.2017.12.024](https://doi.org/10.1016/j.carbpol.2017.12.024).
- [27] Z. Hussain, W. Sajjad, T. Khan, F. Wahid, Production of bacterial cellulose from industrial wastes: a review. *Cellulose* 26 (2019) 2895–2911. [doi:10.1007/s10570-019-02307-1](https://doi.org/10.1007/s10570-019-02307-1).
- [28] R. Wu, X. Zhao, D. Liu, Structural Features of Formiline Pretreated Sugar Cane Bagasse and Their Impact on the Enzymatic Hydrolysis of Cellulose. *ACS Sustain. Chem. Eng.* 4 (2016) 1255-1261. <https://doi.org/10.1021/acssuschemeng.5b01298>.

- [29] T. Lu, M. Jiang, Z. Jiang, D. Hui, Z. Wang, Z. Zhou, Effect of surface modification of bamboo cellulose fibers on mechanical properties of cellulose/epoxy composites. *Compos. Part B Eng.* 51 (2013) 28-34. <https://doi:10.1016/j.compositesb.2013.02.031>.
- [30] J.P. Reddy, J.W. Rhim. Characterization of bionanocomposite films prepared with agar and paper-mulberry pulp nanocellulose. *Carbohydr. Polym.* 110 (2014) 480-488. <https://doi:10.1016/j.carbpol.2014.04.056>.
- [31] A.D. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D.V. Templeton, D. Croker, Determination of Structural Carbohydrates and Lignin in Biomass NREL.
- [32] F. Lu, H. Yu, C. Yan, J. Yao, Polylactic acid nanocomposite films with spherical nanocelluloses as efficient nucleation agents: effects on crystallization, mechanical and thermal properties. *RSC Adv.* 6 (2016) 46008-46018. <https://doi:10.1039/C6RA02736G>.
- [33] H.Y. Yu, Z.Y. Qin, B. Sun, X.G. Yang, J.M. Yao, Reinforcement of transparent poly(3-hydroxybutyrate-co-3-hydroxyvalerate) by incorporation of functionalized carbon nanotubes as a novel bionanocomposite for food packaging. *Compos. Sci. Technol.* 94 (2014) 96-104. <https://doi:10.1016/j.compscitech.2014.01.018>.
- [34] E. Fortunati, M. Peltzer, I. Armentano, L. Torre, A. Jiménez, J.M. Kenny, Effects of modified cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites. *Carbohydr. Polym.* 90 (2012) 948-956. <https://doi:10.1016/j.carbpol.2012.06.025>.
- [35] S. Park, J.O. Baker, M.E. Himmel, P.A. Parilla, D.K. Johnson, Cellulose crystallinity

- index: measurement techniques and their impact on interpreting cellulase performance.
- Biotechnol. Biofuels. 3 (2010) 10. <https://doi:10.1186/1754-6834-3-10>.
- [36] B. Li, W. Xu, D. Kronlund, A. Määttänen, J. Liu, J.H. Smått, J. Peltonen, S. Willför, X. Mu, C. Xu, Cellulose nanocrystals prepared via formic acid hydrolysis followed by TEMPO-mediated oxidation. Carbohydr. Polym. 133 (2015) 605-612. <https://doi:10.1016/j.carbpol.2015.07.033>.
- [37] B. Li, H. Mou, Y. Li, Y. Ni, Synthesis and Thermal Decomposition Behavior of Zircoaluminate Coupling Agents. Ind. Eng. Chem. Res. 52 (2013) 11980-11987. <https://doi:10.1021/ie400888p>.
- [38] Y. Sun, L. Lin, Hydrolysis Behavior of Bamboo Fiber in Formic Acid Reaction System. J. Agric. Food Chem. 58 (2010) 2253-2259. <https://doi:10.1021/jf903731s>.
- [39] M.K.M. Haafiz, A. Hassan, A. Zakaria, I.M. Inuwa, M.S. Islam, M. Jawaid, Properties of polylactic acid composites reinforced with oil palm biomass microcrystalline cellulose. Carbohydr. Polym. 98 (2013) 139-145. <https://doi:10.1016/j.carbpol.2013.05.069>.
- [40] J. Yu, Z. Qiu. Preparation and Properties of Biodegradable Poly(L-lactide)/Octamethyl-Polyhedral Oligomeric Silsesquioxanes Nanocomposites with Enhanced Crystallization Rate via Simple Melt Compounding. ACS Appl. Mater. Interfaces 3 (2011) 890-897. <https://doi:10.1021/am1012485>.
- [41] C. Xu, J. Chen, D. Wu, Y. Chen, Q. Lv, M. Wang, Polylactide/acetylated nanocrystalline cellulose composites prepared by a continuous route: A phase

- interface-property relation study. *Carbohydr. Polym.* 146 (2016) 58-66.
<https://doi.org/10.1016/j.carbpol.2016.03.058>.
- [42] J. Zhao, X. He, Y. Wang, W. Zhang, X. Zhang, X. Zhang, Y. Deng, C. Lu,
 Reinforcement of all-cellulose nanocomposite films using native cellulose nanofibrils.
Carbohydr. Polym. 104 (2014) 143-150. <https://doi.org/10.1016/j.carbpol.2014.01.007>.
- [43] A. Jiménez, M.J. Fabra, P. Talens, A. Chiralt, Effect of re-crystallization on tensile,
 optical and water vapour barrier properties of corn starch films containing fatty acids.
Food Hydrocoll. 26 (2012) 302-310. <https://doi.org/10.1016/j.foodhyd.2011.06.009>.
- [44] L. Coltro, J. Borghetti, Plastic packages for personal care products: evaluation of light
 barrier properties. *Polímeros*. 17 (2007) 50-61.
<https://doi.org/10.1590/S0104-14282007000100013>.
- [45] A.A. Oun, J.W. Rhim, Preparation and characterization of sodium carboxymethyl
 cellulose/cotton linter cellulose nanofibril composite films. *Carbohydr. Polym.* 127
 (2015) 101-109. <https://doi.org/10.1016/j.carbpol.2015.03.073>.
- [46] P. Rytlewski, M. Stepczyńska, U. Gohs, R. Malinowski, B. Budner, M. Żenkiewicz,
 Flax fibres reinforced polylactide modified by ionizing radiation. *Ind. Crops Prod.* 112
 (2018) 716-723. <https://doi.org/10.1016/j.indcrop.2018.01.004>.
- [47] G. Gorrasi, R. Pantani, M. Murariu, P. Dubois, PLA/Halloysite Nanocomposite Films:
 Water Vapor Barrier Properties and Specific Key Characteristics. *Macromol. Mater.*
Eng. 299 (2014) 104-115. <https://doi.org/10.1002/mame.201200424>.

Table 1 Amount (%) of formyl groups formed in formyl cellulose (FC) under different reaction conditions.

Temperature	Formic acid concentration	1 h	2 h	3 h	4 h	5 h
70 °C	70 wt%	1.68±0.18	1.91±0.22	2.62±0.12	4.23±0.15	5.06±0.15
	80 wt%	2.36±0.18	3.73±0.17	4.93±0.21	5.60±0.20	6.61±0.21
	90 wt%	7.03±0.28	8.31±0.21	9.29±0.23	10.01±0.28	10.53±0.21
80 °C	70 wt%	2.54±0.37	3.72±0.16	4.57±0.15	4.99±0.15	5.68±0.23
	80 wt%	2.47±0.07	4.43±0.36	5.35±0.14	5.91±0.20	7.13±0.17
	90 wt%	6.22±0.30	10.94±0.24	11.06±0.23	11.48±0.21	11.78±0.26
90 °C	70 wt%	2.54±0.15	3.72±0.33	4.37±0.27	4.99±0.21	5.68±0.27
	80 wt%	4.02±0.21	5.39±0.21	7.04±0.27	8.11±0.23	9.22±0.28
	90 wt%	7.20±0.28	10.35±0.24	12.82±0.54	14.55±0.33	15.79±0.21

Table 2 Yield (%) of formyl cellulose (FC) under different reaction conditions.

Temperature	Formic acid concentration	1h	2h	3h	4h	5h
70 °C	70 wt%	96.88±2.9	94.44±1.2	93.95±1.9	92.10±2.3	91.03±3.0
	80 wt%	96.88±2.4	95.48±1.6	95.32±1.7	95.28±1.0	91.03±1.9
	90 wt%	96.88±2.4	95.48±1.6	95.32±1.7	95.28±1.0	91.03±1.9

		5	7	8	2	1
	90 wt%	94.20±1.3	93.01±1.6	92.81±2.3	91.58±2.5	89.90±1.9
		3	5	7	6	7
80 °C	70 wt%	95.25±1.1	94.63±2.1	93.29±1.8	91.84±1.3	90.46±1.6
		3	7	2	1	8
	80 wt%	93.99±2.0	93.64±1.2	92.56±1.6	91.05±3.1	90.09±2.3
		7	2	1	8	6
	90 wt%	93.06±1.5	92.64±1.6	90.55±2.3	89.47±2.5	88.09±1.9
		5	5	7	6	7
90 °C	70 wt%	92.99±2.2	91.72±2.2	90.35±1.6	88.70±3.0	96.47±2.7
		9	5	9	7	9
	80 wt%	94.41±2.1	92.94±2.4	90.47±1.6	87.95±1.9	84.35±2.0
		9	0	6	7	5
	90 wt%	90.99±1.3	89.66±1.8	87.55±2.2	56.20±1.3	81.54±2.4
		5	3	2	5	3

Table 3 CI of unmodified cellulose and formyl cellulose (FC).

Formyl							
groups	0%	1.68%	2.32%	5.91%	7.19%	11.78%	15.79%
CI (%)	67.16±1.	61.74±2.	62.26±1.	64.36±1.	64.73±2.	65.03±1.	66.79±1.
	61	03	41	23	16	24	57

Table 4 Crystallinity index (CI) of PLA and PLA/formyl cellulose (FC) composite films.

Formyl							
1	0%	1.68%	2.32%	5.91%	7.19%	11.78	15.79%
						%	
groups							
CI (%)	31.82±0.6	31.89±1.1	33.93±0.7	36.51±0.9	39.19±0.5	40.22	42.92±1.0
	8	2	5	1	5	±93	5

Figure 1 SEM image of unmodified cellulose (a) and formyl cellulose (FC) with 15.79% formyl groups (b).

Figure 2 Particle size distribution of formyl cellulose (FC) with 15.79% formyl groups.

Figure 3 FTIR spectra for unmodified cellulose (a) and formyl cellulose (FC) samples with different amounts of formyl groups (b–g: 1.68%, 2.32%, 5.91%, 7.19%, 11.78%, and 15.79%).

Figure 4 SEM image of PLA film (a) and PLA composite films containing 1 wt% formyl cellulose (FC) with different amounts of formyl groups (b–g: 1.68%, 2.32%, 5.91%, 7.19%, 11.78%, and 15.79%).

Figure 5 FTIR spectra for PLA film (a) and PLA/formyl cellulose (FC) composite films containing 1 wt% FC with different amounts of formyl groups (b–g: 1.68%, 2.32%, 5.91%, 7.19%, 11.78%, and 15.79%).

Figure 6 X-ray diffractograms for PLA film (a) and PLA/formyl cellulose (FC) composite films containing FC with different amounts of formyl groups (b–g: 1.68%, 2.32%, 5.91%, 7.19%, 11.78%, and 15.79%).

Figure 7 Tensile strength, elongation at break, and Young's modulus of PLA and PLA/formyl cellulose (FC) composite films.

Figure 8 Light transmittance of PLA and PLA/formyl cellulose (FC) composite films.

Figure 9 Water absorption (WA) of PLA and PLA/formyl cellulose (FC) composite films.

Figure 10 Water vapor permittivity (WVP) of PLA and PLA/formyl cellulose (FC) composite films.

CRedit author statement:

Shuangyan Long: Conceptualization, Methodology, Validation, Formal Analysis, Investigation, Data Curation. **Lei Zhong:** Writing - Original Draft, Writing - Review & Editing. **Xuliang Lin:** Methodology. **Xiaogang Chang:** Investigation. **Fuqi Wu:** Visualisation. **Ruchun Wu:** Conceptualization, Methodology, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Supervision, Project administration, Funding acquisition. **Fengwei Xie:** Visualisation, Writing - Review & Editing.

Highlights:

- ✓ Formyl cellulose prepared by a simple method was used to reinforce PLA
- ✓ Formylation degree controlled by temperature, time and formic acid concentration
- ✓ Formyl cellulose improved the mechanical and water-barrier properties of PLA
- ✓ Formate groups improves cellulose compatibility with PLA
- ✓ PLA/formyl cellulose composites potential for food packaging