### SUPPLEMENTARY DOCUMENT

# Integrated Design of Multifunctional Reinforced Bioplastics (MReB) to Synergistically Enhance Strength, Degradability, and Functionality

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#### Supplementary Note 1: Models for designing bioplastic composites



Figure S1. The schematic diagrams of reinforced plastic composites. (a) Particulate reinforced plastic composite. (b) Short fiber reinforced plastic composite. (c) Multi-layer reinforced plastic composite.

In Figure S1a, the stiffness of a pure polymer matrix can be effectively enhanced by incorporating particles with high stiffness. The elastic modulus of particulate reinforced composites can be predicted using eq. (S1):

$$E_{cp} = \alpha E_p V_p + E_m (1 - V_p) \quad (S1)$$

Where,  $\alpha$  represents the particle reinforcing factor for the modulus of the particulate composite, which ranges between 0 and 1 based on the particle properties. The  $E_p$  is the modulus of particles,  $E_m$  is the modulus of polymer matrix, and  $V_p$  is the particle volume fraction.

Compared to the rule-of-mixture equation of particulate reinforced plastic composite, the design model of short fiber reinforced plastic composite (Figure S1b) could be evaluated based on laminate analogy approach<sup>1</sup>, thus the in-plane elastic modulus of the short fiber reinforced plastic composite could be calculated by eq. (S2).

$$E_{fp} = E_f \left[ 1 - \frac{e^{\beta L} - 1}{\frac{\beta L}{2} (e^{\beta L} + 1)} \right] V_f + E_m (1 - V_f)$$
(S2)

In this equation,  $E_f$  represents the modulus of short fiber, L is the average fiber length,  $E_m$  is the modulus of polymer matrix, and  $V_f$  is the short fiber volume fraction.  $\beta$  is calculated by the eq. S3 <sup>2, 3</sup>.

$$\beta = \left[\frac{2G_m}{E_f r_f^2 In\left(\frac{R}{r_f}\right)}\right]^{1/2}$$
(S3)

Here,  $G_m$  is the shear modulus of the matrix, and R is the mean separation of the fibers normalized to their length.

The modulus of composite materials is influenced by various factors, including the modulus of the reinforcing material, the volume fraction of the reinforcement, its shape, and the reduced coefficient of the reinforced materials. This is illustrated by comparison of eq. S1 for particulate reinforced plastic composites and eq. S2 for short fiber reinforced plastic composites. Our findings indicate that the biobased particle reinforcements with lignin<sup>4</sup> and starch<sup>5</sup> exhibit lower reinforcement efficiency for plastic composites compared to cellulose<sup>6</sup> because the lignin and starch reinforcements have lower modulus and geometry reduction. Therefore, cellulose is suggested as one of optimal reinforcing agents for plastic composites.

Eq. S2 and eq. S3 demonstrate the significant impact of the fiber length to diameter ratio on the reduction factor and modulus of the as-designed composite. Increasing the fiber length to diameter ratio results in a meaningfully improvement in the as-designed modulus of composite material. Additionally, the modulus of fiber dramatically increases as the fiber diameter decrease<sup>6</sup>. Consequently, a processed cellulose nanofiber(CNF) with a larger length to diameter ratio and higher modulus than unprocessed cellulose was employed in the design and fabrication of the CNF-reinforced plastic composite film<sup>7, 8</sup>.

Despite the cellulose is an optimal reinforcement for plastic composites according to the aforementioned design models, its hydrophilic property can limit the strengths of as-designed composites due to the incompatibility with the hydrophobic plastics matrix. Therefore, the further chemical modification of cellulose is necessary to achieve better material performance. To address the design challenge, a multi-layer design concept was applied to the CNF-reinforced plastic composite (Figure S2). First, the CNF, with its rich flexible hydroxyl groups, forms a self-assemble layer through the hydrogen bonding. Second, the plastic layer laminated on the sides of CNF layer can further improve the surface functionality, such as degradability, water stability, printability, and air permeable resistance. Third, the CNF layer could significantly reinforce the strength of the plastic composite film.

The design configuration of PHB/CNF multi-layer reinforced plastic composite is shown in Figure S2. To address the interfacial premature debonding issue, the crosslinker TDI has been specifically formulated to ensure strong bonding between the CNF layer and plastic layer in the composite. The modulus of the PHB/CNF/TDI multilayer plastic composite can be calculated by the Eq. (S4).

$$E_{PHB|CNF|TDI} = \gamma (E_{cc}r + E_{pc} - rE_{pc})$$
(S4)

Here,  $E_{PHB|CNF|TDI}$  represents the modulus of the PHB/CNF/TDI composite.  $\gamma$  is the reduced coefficient determined through the experiments, ranging between 0 to 1.  $E_{cc}$  and  $E_{Pc}$  are the moduli of the CNF layer and PHB layer respectively. The relative thickness fraction of the CNF layer and PHB layer is denoted as

r, which is equal to  $\overline{t}$ .  $t_c$  represents the thickness of CNF layer in the plastic composite and t is the total thickness of the plastic composite.



Figure S2. The design configuration of the MReB (PHB/CNF/TDI) multi-layer composite film.

Table S1 The comparison of modulus of the MReB	(PHB/CNF/TDI) multi-layer composite film
through the experime	nts and models

Samples ID	Tensile	Tensile	Error
	modulus	modulus	(%)
	GPa	GPa	
	(Experiment)	(Model)	
PHB/CNF/TDI	4.63	4.42	4.5

Note: The density of cellulose is 1.60 g/cm<sup>3</sup> and the density of PHB is 1.25 g/cm<sup>3</sup>. The tensile modulus result was calculated using Equation S4, with the modulus of each component obtained from

experimental data. The thickness of the sample was measured using SEM images. The coefficients of  $\gamma_E$  for the PHB/CNF/TDI film is 0.6 based on experimental results.

t<sub>c</sub>

# Supplementary note 2: Permeability of the bioplastic composites

Sample ID	Thickness (mm)	RH (%)	Temp. (C°)	Oxygen transmission rate (OTR) (ml·m <sup>-2</sup> ·d <sup>-1</sup> )	Oxygen permeance (PO2) (ml·m <sup>-2</sup> ·d <sup>-1</sup> ·bar <sup>-</sup> <sup>1</sup> )	Oxygen permeability coefficient (P'O2) (ml·mm·m <sup>-2</sup> ·d <sup>-</sup> <sup>1.</sup> bar <sup>-1</sup> )
CNF	$0.45 \pm 0.05$	0%	23	$0.3180 \pm 0.0120$	$0.3138 \pm 0.1184$	0.1554±0.0125
PHB/CNF	$0.79{\pm}0.08$	0%	23	$0.1510 \pm 0.0363$	$0.1490 {\pm} 0.3581$	$0.1099 \pm 0.0279$
PHB/CNF/TDI	$0.74 \pm 0.07$	0%	23	0.1235±0.0106	0.1219±0.0105	$0.0909 \pm 0.0088$

Table S2.	Oxygen	permeability	results
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Note: a is standard derivation.

Table S3.	Comparison	of oxygen	permeability	coefficient	of different	polymer films

Polymers	Oxygen permeability coefficient at 0%RH and 23 C° (ml·mm·m <sup>-2</sup> ·d <sup>-1</sup> ·atm <sup>-1</sup> )	Ref.
PHB/CNF/TDI	$0.0914{\pm}0.0084$	This work
Poly (ethylene terephthalate) (PET)	1	9
Polypropylene (PP)	50	9
Polyethylene (PE)	50	9
Polystyrene (PS)	100	9
Poly lactic acid (PLA)	9.3-18.1	10, 11
Poly (vinyl chloride) (PVC)	2	9
Polyhydroxybutyrate (PHB)	4.6	10
(PLA)/(PHB)=85:15	8.4	11

## Supplementary note 3: Comparison of mechanical properties

Table S4. The comparison of the composite material from this study to PHB-based composite and common petrochemical materials in relevant studies.

Material	Tensile strength	Elastic Modulus	Method	Reference
	(MPa)	(GPa)		
PHB/CNF/TDI	21.5	4.63	TDI cross-linking	This work
PHB-Clay Composite	28.72	2.33	PHB/bentonite compositing	12
PHB-PP Blend	24.5	1.88	PHB-PP blending	13
PHB-Bamboo fiber	9.73-12.05	1.044-2.165	Molding and Extrusion	14
PHB-agave fiber	19.5-26	0.9-2.3	Molding and Extrusion	15
10%PHB-PLA	49.9	2.48	Molding and Extrusion	16
30%PHB-corn	7.98-14.6	0.78-1.62	Plasma treatment and	17
strach			extrusion	
25%-75%PHB- PBAT	10-16	0.326-0.536	Molding and Extrusion	18
PHB-1%-5%CNF	10.6-31.2	1.4-1.97	Solvation process	19
PHB-1%-5%CNC	27.1-31.2	1.7-2.0	Solvation process	19

### Supplementary note 4: TDI residue analysis by GCMS

The 50mg of PHB/CNF/TDI film was cut into 2mm×1mm pieces and immersed in 500uL hexane stirring for 4 hours (Figure S3). The elute was analyzed by gas-chromatography mass spectrometry (GC/MS) (SHIMADZU GCMS-QP2010 SE) with Zebron ZB-35HT Inferno GC (Phenomenex, CA) column in split mode. Helium was used as the carrier gas. The injection temperature was set to 260°C. The GC-MS program was first held at 40 °C for 30 seconds, then increased at a rate of 20 °C/min to 120 °C, then at a rate of 5 °C/min to 200 °C, then at a rate of 20 °C/min to 260 °C, then at a rate of 5 °C/min to 310 °C, and finally hold for 3 min. The control data were established using 1 ppm, 20 ppm, 50 ppm, and 100 ppm TDI solutions, tested by GCMS using the same method, respectively. The 1ppm concentrated TDI solution was not detected by GCMS. The spectra of 100ppm, 50ppm, and 20ppm TDI control samples, TDI standard test curve, and the spectrum of PHB/CNF/TDI residue sample are shown in Figure S3 (b), (c) and (d), it indicates that no TDI residue from the PHB/CNF/TDI films was detected by GCMS. This finding suggests that TDI completely reacted with CNF and PHB components. Moreover, the XPS spectra of PHB/CNF/TDI confirmed that the full reaction of components with the TDI crosslinker. Notably, the multi-layer design provides additional assurance by effectively containing the TDI within the interlayers, thereby eliminating any safety concerns related to the TDI release.



Figure S3. (a) PHB/CNF/TDI (MReB) sample preparation for TDI residue test; (b) Standard spectra of 100 ppm, 50 ppm, and 20 ppm TDI solutions by GC/MS; (c) TDI standard test curve calculated by the peak areas. (d) TDI residue test of PHB/CNF/TDI (MReB) by GCMS, showing no detectable TDI in the spectrum.



Figure S4. XPS spectra of composite films: (a). Scanned spectra of CNF; (b) C1s XPS spectra of CNF; (c) scanned spectra scan of PHB/CNF/TDI (MReB); (d). C1s XPS spectra of PHB/CNF/TDI (MReB).



Figure S5. Storage modulus curves of CNF, PHB/CNF, and PHB/CNF/TDI(MReB) composites



Figure S6 The surface morphologies of composite films: (a). CNF; (b) PHB/CNF/TDI (MReB).

(b)

Phase

1.0 μm

Height Sensor



0 hour

2 hours

24 hours

Figure S7. The observation images of the CNF straw and MReB straw in water from 0 to 24 hours.



Figure S8. Water absorption of CNF and PHB/CNF/TDI

#### **References:**

- 1. S.-Y. Fu, G. Xu and Y.-W. Mai, *Composites Part B: Engineering*, 2002, **33**, 291-299.
- 2. H. Cox, British journal of applied physics, 1952, **3**, 72.
- 3. S.-Y. Fu and B. Lauke, *Composites Science and Technology*, 1998, **58**, 1961-1972.
- 4. W. Cousins, *Wood science and technology*, 1976, **10**, 9-17.
- 5. B. Madsen, R. Joffe, H. Peltola and K. Nättinen, *Journal of composite materials*, 2011, **45**, 2119-2131.
- 6. S. Iwamoto, W. Kai, A. Isogai and T. Iwata, *Biomacromolecules*, 2009, **10**, 2571-2576.
- 7. J. Li, L. Wei, W. Leng, J. F. Hunt and Z. Cai, *Journal of materials science*, 2018, **53**, 4949-4960.
- 8. J. Li, Q. Yan and Z. Cai, *Cellulose*, 2019, **26**, 1769-1780.
- 9. J. Lange and Y. Wyser, *Packaging Technology and Science: An International Journal*, 2003, **16**, 149-158.
- 10. M. P. Arrieta, 2014.
- 11. N. Burgos, I. Armentano, E. Fortunati, F. Dominici, F. Luzi, S. Fiori, F. Cristofaro, L. Visai, A. Jiménez and J. M. Kenny, *Food and Bioprocess Technology*, 2017, **10**, 770-780.
- 12. T. G. Almeida, L. P. Costa Jr, J. A. M. Agnelli, R. M. R. Wellen, E. L. Canedo and L. H. Carvalho.
- 13. W. M. Pachekoski, J. A. M. Agnelli and L. P. Belem, *Materials research*, 2009, **12**, 159-164.
- 14. R. Krishnaprasad, N. Veena, H. J. Maria, R. Rajan, M. Skrifvars and K. Joseph, *Journal of Polymers and the Environment*, 2009, **17**, 109-114.
- 15. M. K. M. Smith, D. M. Paleri, M. Abdelwahab, D. F. Mielewski, M. Misra and A. K. Mohanty, *Green Chemistry*, 2020, **22**, 3906-3916.
- 16. J. C. C. Yeo, J. K. Muiruri, B. H. Tan, W. Thitsartarn, J. Kong, X. Zhang, Z. Li and C. He, ACS Sustainable Chemistry & Engineering, 2018, **6**, 15517-15527.
- 17. J. P. Florez, M. Fazeli and R. A. Simão, *International journal of biological macromolecules*, 2019, **123**, 609-621.
- 18. R. Hoffmann, D. D. S. Morais, C. J. F. Braz, K. Haag, R. M. R. Wellen, E. L. Canedo, L. H. De Carvalho and K. Koschek, *Composites Part A: Applied Science and Manufacturing*, 2019, **124**, 105472.
- 19. B. Zhang, C. Huang, H. Zhao, J. Wang, C. Yin, L. Zhang and Y. Zhao, *Polymers*, 2019, **11**, 2063.