



Title	Improving the mechanical properties of polycaprolactone using functionalized nanofibrillated bacterial cellulose with high dispersibility and long fiber length as a reinforcement material
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Citation	Composites Part A: Applied Science and Manufacturing, 158, 106978 https://doi.org/10.1016/j.compositesa.2022.106978
Issue Date	2022-07
Doc URL	http://hdl.handle.net/2115/92942
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Supporting Information

Improving the mechanical properties of polycaprolactone using functionalized nanofibrillated bacterial cellulose with high dispersibility and long fiber length as a reinforcement material

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Number of pages: 14

Number of figures: 12

Number of tables: 2

Number of equations: 6

1. Materials

Never-dried nanofibrillated bacterial cellulose produced using hydroxypropylcellulose (HPC) (HP-NFBC) was supplied by Kusano Sakko Inc. HP-NFBC was washed three times with distilled water. The mixture was subsequently centrifuged several times (12000 rpm, 25 °C, 10 min) to remove all impurities. After freezing at −80 °C for 2 h, the purified HP-NFBC was lyophilized for 48 h. Thereafter, the HP-NFBCs were dried in an oven at 105 °C for 2 h to remove adsorbed water molecules prior to their use in the experiments.

2. Structural analyses of HP-NFBC

2.1. Determination of cellulose content

The freeze-dried HP-NFBC (30–40 mg) was placed in a screw-capped test tube and dried in an oven at 105 °C for 5 h. Thereafter, the screw-capped test tube containing the freeze-dried HP-NFBC was removed from the oven and placed in a desiccator under vacuum for 20 min to allow the sample to cool to room temperature. Next, 3 mL of 60 % tetrabutylphosphonium hydroxide [TBPH: Hokko Chemical Industry Co., Ltd. (Tokyo, Japan)] was added to the test tube and stirred at 30 °C for 17 h. After the freeze-dried HP-NFBC was fully dissolved, Milli-Q water (100 mL) was added and stirred for 30 min to precipitate the cellulose. After collecting the precipitate formed by filtration, the filter paper containing the precipitate (cellulose) was dried at 105 °C for 2 h in an oven. The filter paper with the precipitate was then placed in a desiccator under vacuum for 20 min and weighed.

2.2. Determination of cellulose concentration

The weight of an empty Petri dish was measured before placing the never-dried HP-NFBC sample (5–10 g) in the dish. Thereafter, the Petri dish containing the sample was placed in a 105 °C drying oven for 5 h. After 5 h, the Petri dish was removed from the oven and cooled to room temperature under vacuum in a desiccator. The weight of the Petri dish containing the dried HP-NFBC was measured, and the cellulose concentration was calculated using the following equation :

$$\text{Concentration (wt. \%)} = \frac{W_{0,\text{total}} - W_{\text{petri}}}{W_{d,\text{total}} - W_{\text{petri}}} \times 100$$

where $W_{0,\text{total}}$, $W_{d,\text{total}}$ and W_{petri} are the weights of the Petri dish containing the never-dried NFBC, dried NFBC and the empty Petri dish, respectively.

2.3. Transmittance measurements

Transmittance measurements were performed using a spectrophotometer (HITACHI, U-2001) using a semi-micropolystyrene-based plastic cuvette to estimate the dispersibility of HP-NFBC in water. Milli-Q water was added to each never-dried HP-NFBC sample to achieve a concentration of 0.1 wt.%. The transparency of the HP-NFBC suspension was measured at 500 nm.

2.4. Fourier-transform infrared (FT-IR) spectroscopy

FT-IR spectroscopy analyses were performed using an FT-IR spectrophotometer (JASCO, FT/IR- 4200) by the transmission method. The sample suspension (20 μL) was dropped onto a Si substrate and dried completely. After the measurement, baseline correction was performed, and the spectrum was normalized based on the peak (1161.9 cm^{-1}) derived from the C–O stretching of the glycosidic bond.

2.5. Atomic force microscopy (AFM) observation

AFM images were obtained using a HITACHI AFM5000II instrument in tapping mode with a silicon cantilever (SI-DF3P2, SII Nanotechnology Inc.) having a resonant frequency and spring constant of 70 kHz and 2.1 Nm^{-1} , respectively. Each HP-NFBC sample was dispersed in Milli-Q water (0.05 wt.%) and then dried at 30 °C in a drying oven before being subjected to AFM observation.

3. Characterization of HP-NFBC

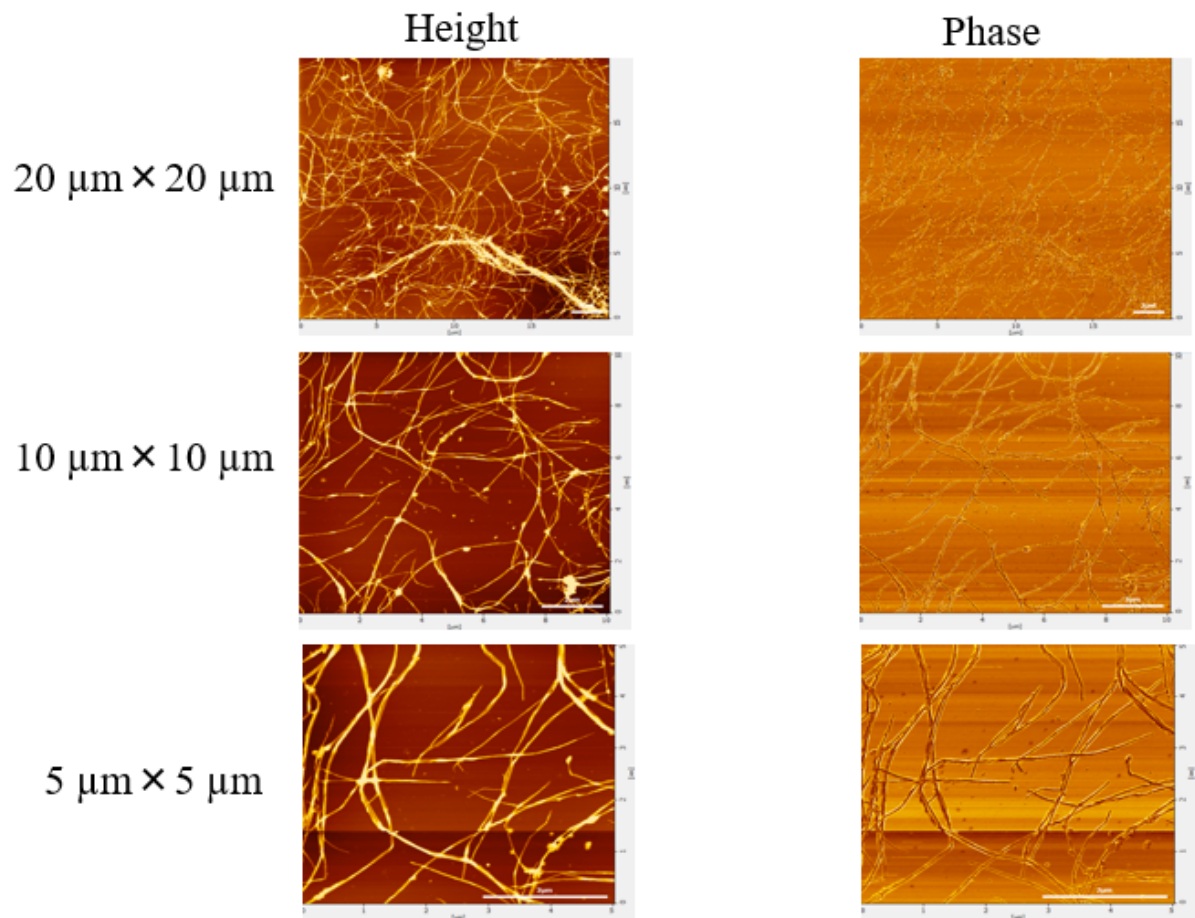


Figure S1. AFM images of HP-NFBC, left: height; right: phase.

4. Confirmation of polymerization reaction

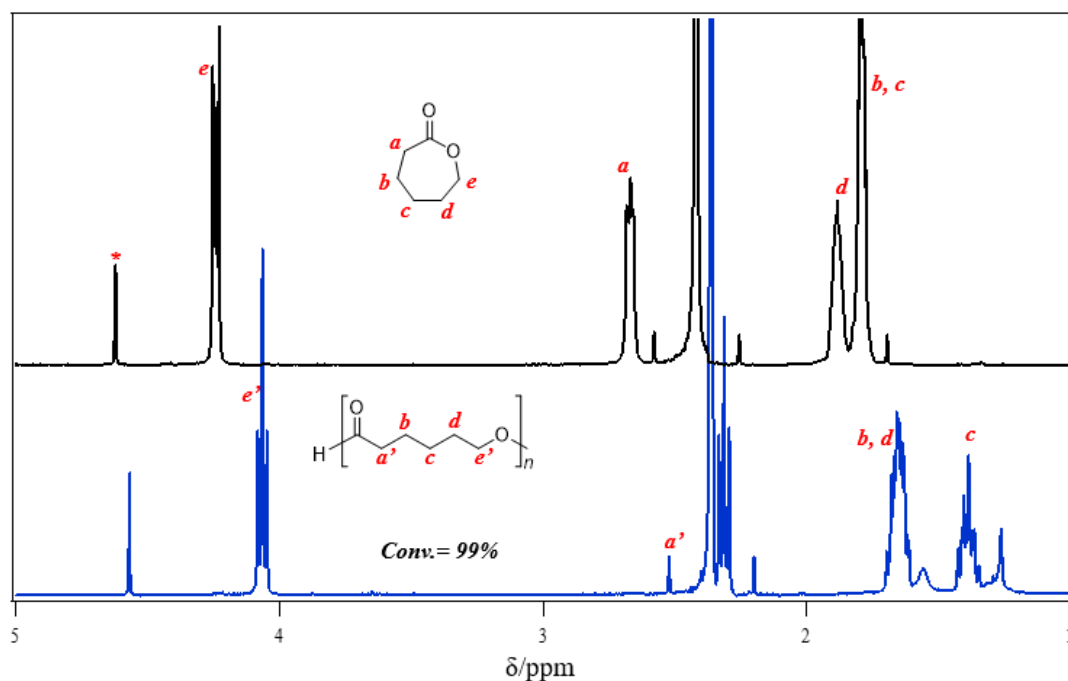


Figure S2. ^1H NMR spectra of HPNFBC-g-PCL-20 before addition of a catalyst (upper) and quench of polymerization (lower) (spectra were recorded in CDCl_3 , operating frequency: 400 MHz).(*internal standard: dibenzyl ether).

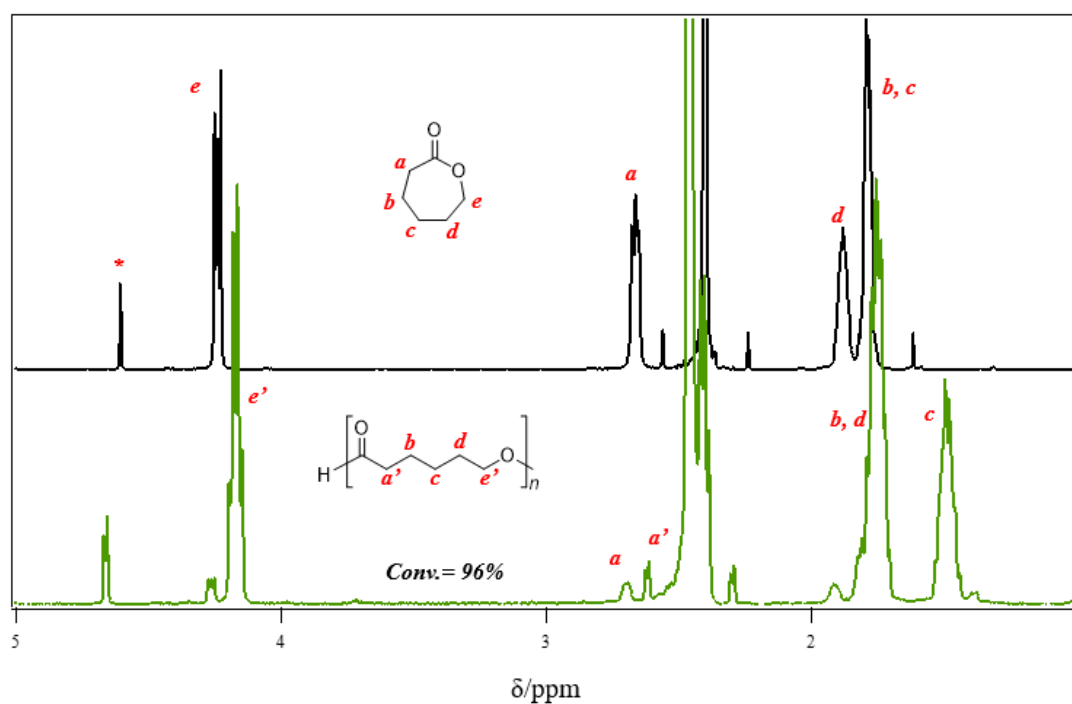


Figure S3. ^1H NMR spectra of HPNFBC-g-PCL-15 before addition of a catalyst (upper) and quench of polymerization (lower) (spectra were recorded in CDCl_3 , operating frequency: 400 MHz).(*internal standard: dibenzyl ether).

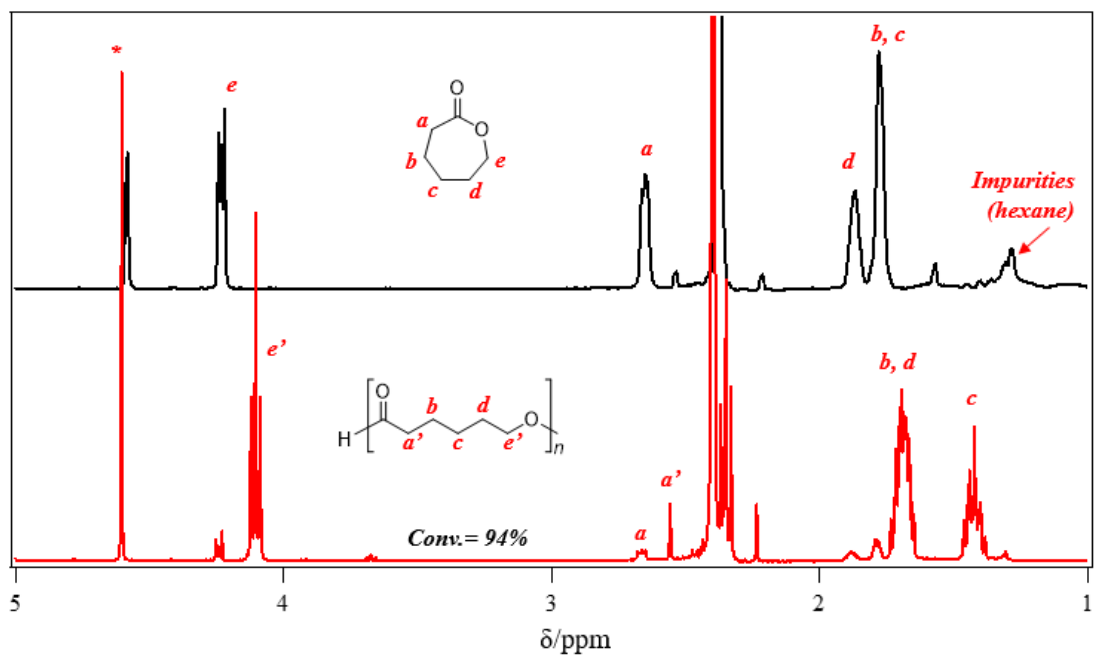


Figure S4. ¹H NMR spectra of HPNFBC-g-PCL-10 before addition of a catalyst (upper) and quench of polymerization (lower) (spectra were recorded in CDCl₃, operating frequency: 400 MHz).(*internal standard: dibenzyl ether).

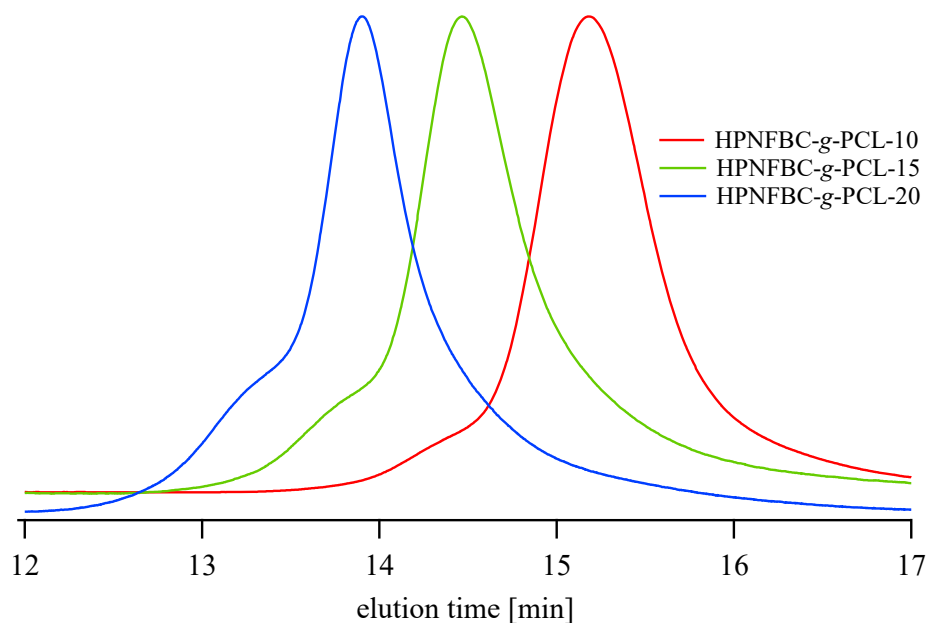


Figure S5. SEC traces of un-grafted PCL homopolymers obtained from the preparation of each HPNFBC-g-PCLs (eluent, THF; flow rate, 1.0 mL min⁻¹, Polystyrene standard.).

5. Determination of coefficient for HP-NFBC and grafted PCL content calculations by CP/MAS

^{13}C NMR.

^{13}C CP/MAS NMR was performed on PCL-grafted HP-NFBC as a function of the contact time to extract the maximum magnetization through cross polarization (CP) transfer without relaxation. **Figure S6** shows the CP time-relative magnetization graph obtained through NMR relaxation time experiment. Linear approximation of semi-log was plotted using the points obtained to calculate the coefficient from the extrapolation (**Figure S7** and **Table S1**). PCL C_{b-e} and HP-NFBC C_1 were chosen for the content calculation as both peaks are not overlaying with any other peaks.

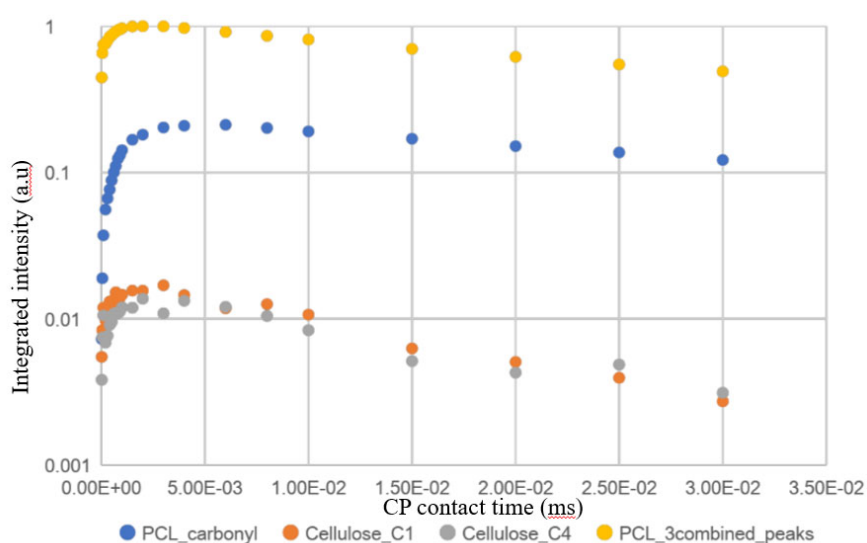


Figure S6. CP time-relative magnetization graph obtained through NMR relaxation time experiment.

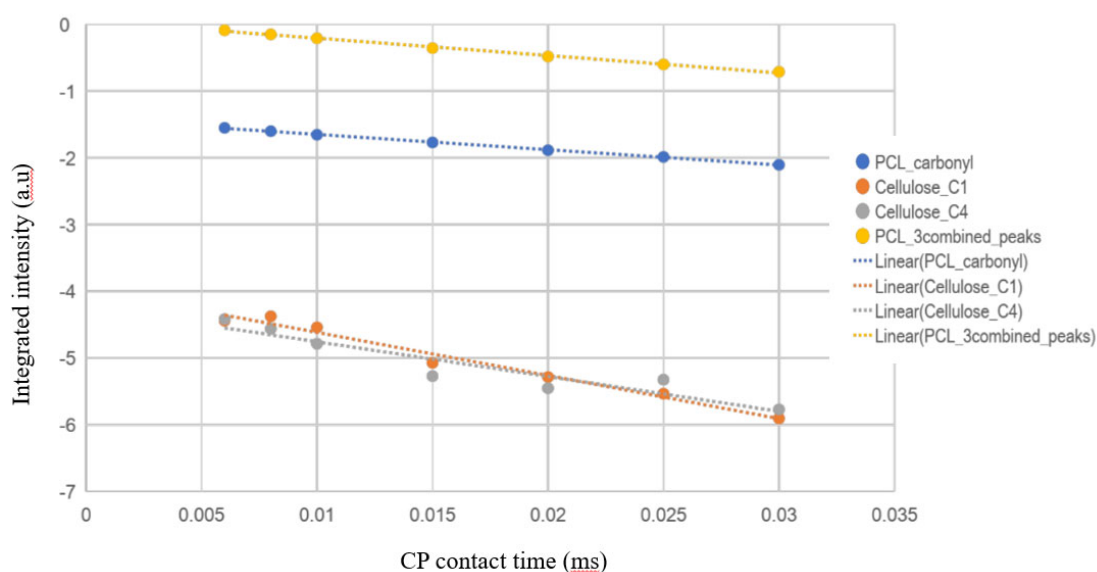
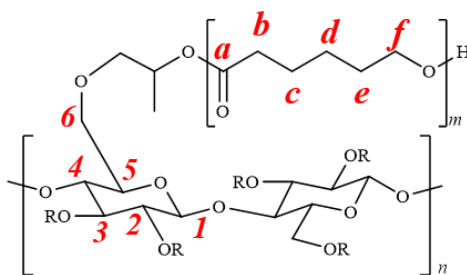


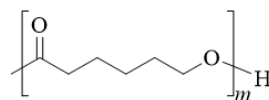
Figure S7. Linear approximation of semi-log of points in **Figure S6**.

Table S1. Coefficients obtained from the extrapolation of the plots in **Figure S7**.

Sample	PCL C _a	HP-NFBC C ₁	HP-NFBC C ₄	PCL C _{b-e}
Coefficient	1.588	1.207	1.130	1.028



R = -H or -CH₂CH(CH₃)OH or



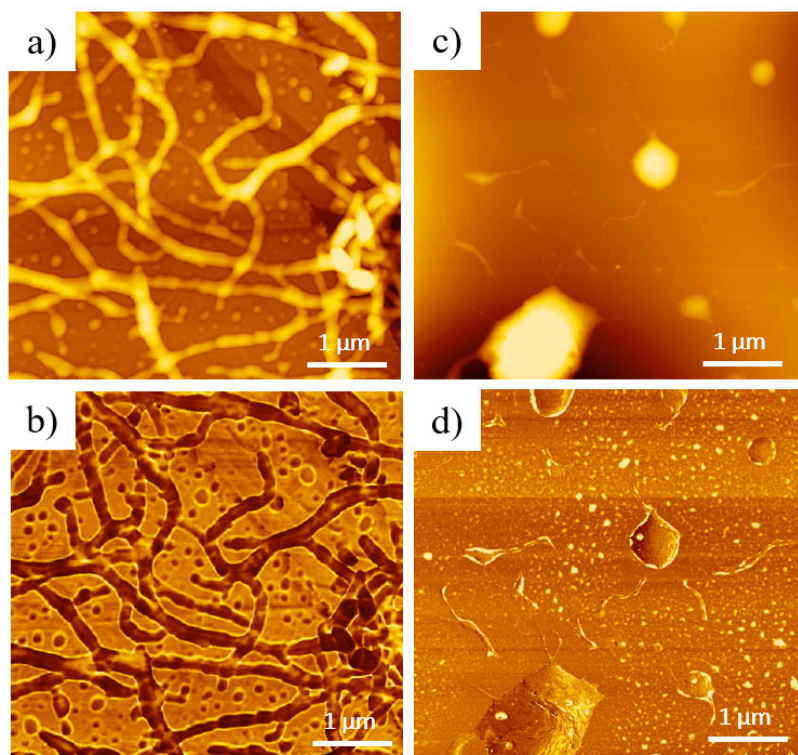


Figure S8. AFM images of HPNFBC-g-PCL-15 (a, height; b, phase) and HPNFBC-g-PCL-10 (c, height; d, phase).

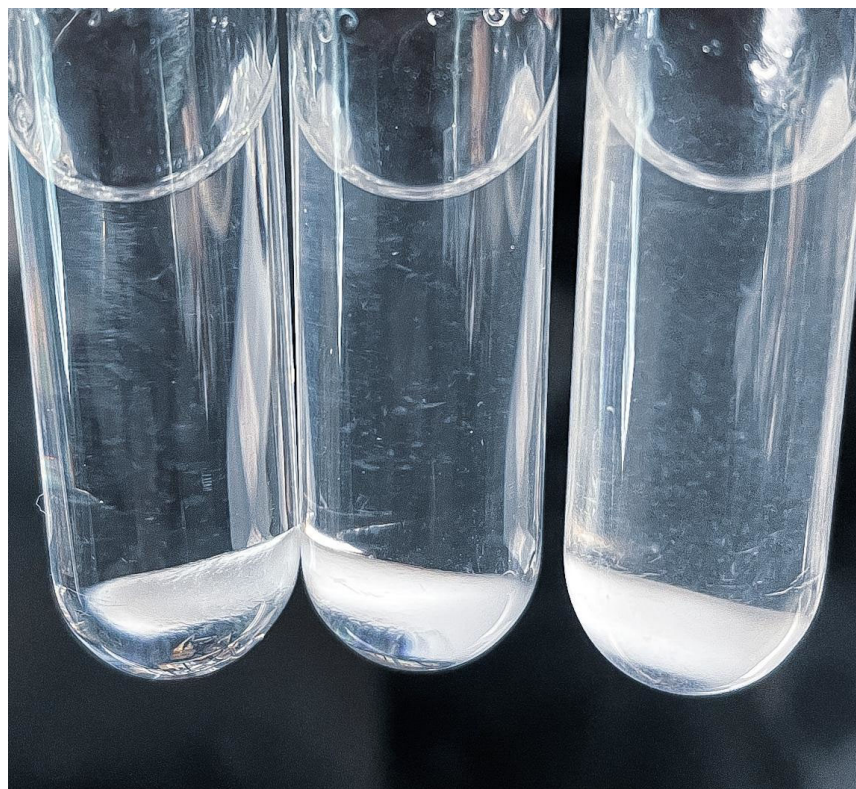


Figure S9. Dispersibility of HPNFBC-g-PCL-20 (left), HPNFBC-g-PCL-15 (middle), and HPNFBC-g-PCL-10 (right) in toluene.

Table S2. Thermal properties of HPNFBC-g-PCL/PCL nanocomposite films.

Sample	Cellulose content (wt. %)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	χ_c (%)
HPNFBC-g-PCL- 20/PCL	1	55.8	43.8	34.5	32.5
	4	55.7	43.6	34.8	33.4
	7	55.5	39.4	34.5	31.2
	13	55.2	45.8	34.7	38.7
HPNFBC-g-PCL- 15/PCL	1	55.8	28.8	35.9	21.3
	4	55.6	46.9	35.0	35.9
	7	55.6	38.8	35.4	30.7
	13	55.5	41.0	35.4	34.7

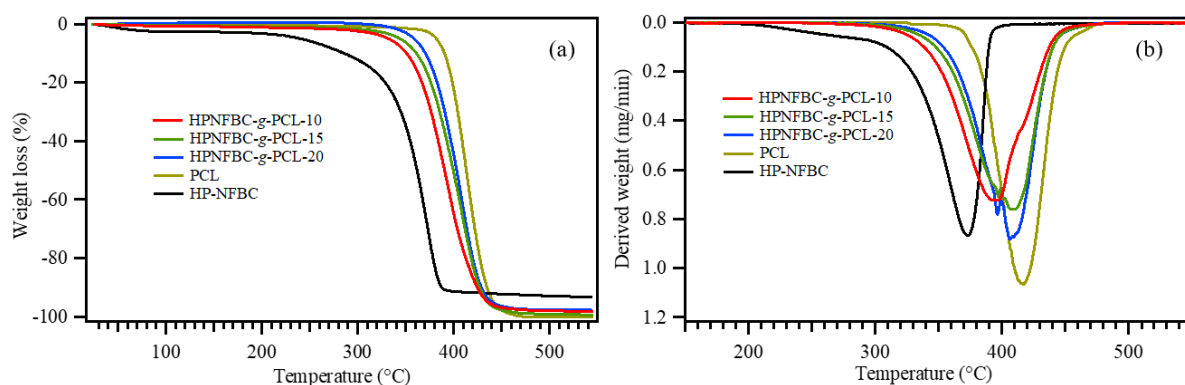


Figure S10. (a) TG and (b) DTG curves of HP-NFBC, PCL-g-HP-NFBCs and PCL (M_n 87400).

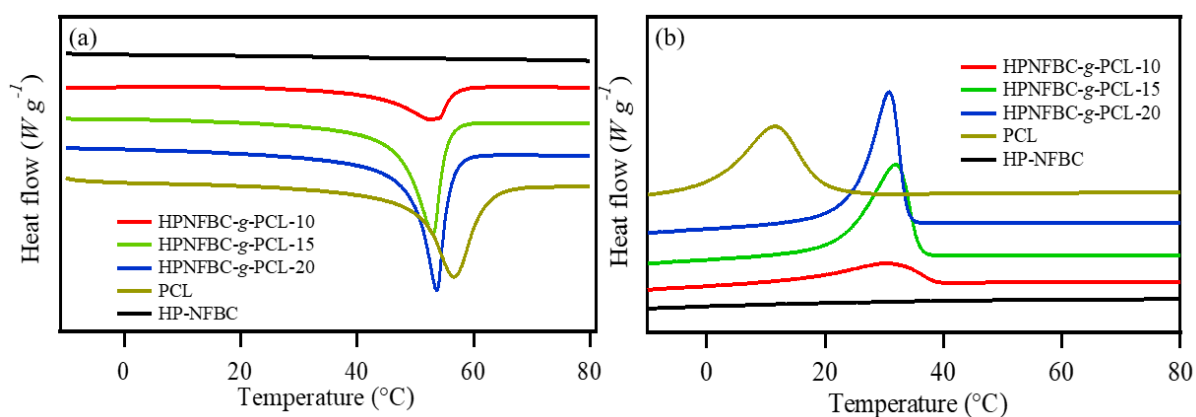


Figure S11. (a) 2nd heating and (b) 1st cooling DSC thermograms of PCL-g-HP-NFBCs, HP-NFBC, and PCL (M_n 87400).

6. Preparation of HPNFBC-g-PCL/PCL nanocomposites.

PCL homopolymer and PCL-grafted HP-NFBC were used as the biodegradable polymer matrix and filler, respectively, because of their similar properties, which resulted in nanocomposites with superior mechanical properties due to the miscibility and favorable interactions between HP-NFBC and PCL. Therefore, PCL and HPNFBC-g-PCL were combined by solvent mixing to produce nanocomposite films. The HP-NFBC contents were calculated based on the HP-NFBC and PCL ratios obtained via solid-state ^{13}C CP/MAS NMR spectroscopy to prepare nanocomposites with 0, 1, 4, 7, and 13 wt.% of cellulose. The

proportions of PCL and HPNFBC-g-PCL used for preparing the blends were calculated from equations S1–S5.

Table S3. Mechanical properties of HP-NFBC/PCL nanocomposites with 13, 7, 4, and 1 wt.% cellulose.

Sample	Cellulose content (wt. %)	Compositions ^a		Ultimate strength ^b (MPa)	Elongation at break ^b (%)	Young's Modulus ^b (MPa)
		HP-NFBC (wt. %)	PCL (wt. %)			
HP-NFBC/PCL	1	1	99	10.9 ± 2.2	178.3 ± 161.3	143.9 ± 14.6
	4	5	95	4.4 ± 0.9	171.7 ± 29.9	62.8 ± 13.1
	7	8	92	4.1 ± 0.9	86.7 ± 42.4	94.7 ± 24.2
	13	15	85	-	-	-

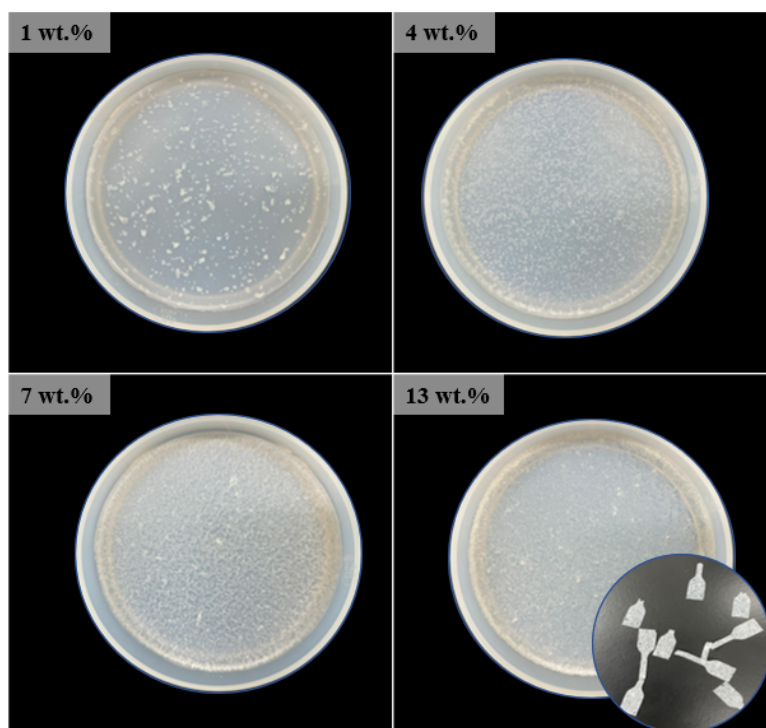


Figure S12 Appearance of HP-NFBC/PCL nanocomposite films.

Equation S1**HP-NFBC content ($C_{\text{HP-NFBC_mol\%}}$) in HPNFBC-g-PCL (mol %)**

PA (C_1) : Peak area of C_1 in cellulose and HPC
 PA (PCL C_{b-e}) : Peak area of C_{b-e} in PCL
 *: coefficient from **Table S1**

$$= \frac{\text{PA}(C_1) \times 1.207}{\text{PA}(C_1) \times 1.207* + \frac{\text{PA}(\text{PCL } C_{b-e})}{4} \times 1.028*} \times 100$$

Equation S2**PCL content ($C_{\text{PCL_mol\%}}$) in HPNFBC-g-PCL (mol %)**

$$= 100 - C_{\text{HP-NFBC_mol\%}}$$

Equation S3**Cellulose content ($C_{\text{cellulose_mol\%}}$) in HPNFBC-g-PCL (mol %)**

HP-NFBC = 75 wt.% cellulose + 25 wt.% HPC
 Molecular weight of 1 unit Cellulose, $M_{w_cellulose} = 162.14$ g/mol
 Molecular weight of 1 unit HPC, $M_{w_HPC} = 336.38$ g/mol

$$= \frac{\frac{0.75}{162.14}}{\frac{0.25}{336.38} + \frac{0.75}{162.14}} \times 100 = 86.2 \text{ mol\%}$$

Equation S4**Cellulose content ($C_{\text{cellulose_wt\%}}$) in HPNFBC-g-PCL (wt.%)**

Molecular weight of 1 unit PCL, $M_{w_PCL} = 114.14$ g/mol
 Molecular weight of 1 unit HP-NFBC, $M_{w_HP-NFBC} = 186.18$ g/mol

$$= \frac{C_{\text{HP-NFBC_mol\%}} \times \text{Molecular weight of 1 unit HP-NFBC, } M_{w_HP-NFBC} \times 0.862}{\left[\frac{C_{\text{PCL_mol\%}} \times \text{Molecular weight of 1 unit PCL, } M_{w_PCL}}{\text{Molecular weight of 1 unit HP-NFBC, } M_{w_HP-NFBC}} \right] + \left[\frac{C_{\text{HP-NFBC_mol\%}} \times \text{Molecular weight of 1 unit HP-NFBC, } M_{w_HP-NFBC}}{\text{Molecular weight of 1 unit HP-NFBC, } M_{w_HP-NFBC}} \right]} \times 100$$

Equation S5**Nanocomposites preparation**

$$\text{HPNFBC-g-PCL weight} = \frac{(\text{Desired cellulose wt.\%} \times \text{total weight of nanocomposites}) / 100}{C_{\text{cellulose_wt\%}}}$$

$$\text{PCL weight} = \text{total weight of nanocomposites} - \text{HPNFBC-g-PCL weight}$$