Supporting Information

Nanocellulose-assisted construction of hydrophilic 3D hierarchical stereocomplex meshworks in enantiomeric polylactides: towards thermotolerant biocomposites with enhanced environmental degradation

Huanhuan Zhang [a, ⊥], Xi Huang [a, ⊥], Chuanfeng Wang [a], Zhou Peng [a], Yali Xu [a], Xuebing He [a], Chaoliang Zhang [c], Jun Lu [a, b, #, *]

[a] Key Laboratory of Advanced Technologies of Materials, Ministry of Education, School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, Sichuan, China
[b] State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, Sichuan, China
[c] State Key Laboratory of Oral Diseases, West China Hospital of Stomatology, Sichuan University, Chengdu 610041, Sichuan, China

[⊥] These authors equally contributed to this work.
[#] Other used names Jun Lv and Jun Lyu.
[*] Corresponding author.
E-mail address: junluprc@hotmail.com (J. Lu).

High-Pressure Experiments and Characterization

Experimental procedure of pressure crystallized PDLA/PLLA/CNCs composites

The pressure and temperature, applied for the crystallization of the PDLA/PLLA/CNCs composites, were according to the P-T phase diagram of PLA by Rohindra et al [1]. The following procedure for crystallization was used. After loading the samples, the temperature was increased to a level to allow them to be fully melted. Then the temperature and pressure were raised to the predetermined level. The samples were kept under these conditions for a predetermined time, and then quenched down to ambient condition. This procedure ensured the minimum degradation of PLA at elevated temperature, and the polymer would be in a molten state before crystallization took place [1, 2].

Characterization

TEM observations were performed using a JEOL JEM-2100F device. WAXD results were obtained at room temperature with a DX-1000 diffractometer using a Cu Kα radiation source in the scanning angle range of 2θ = 5°−50° at a scan speed of 10°/min. After the surface of the samples being etched with configured solution, they were coated with gold for SEM observations using a JSM-6330F apparatus. The contact angles (CAs) of water droplets on the sample surfaces were measured using a KRUSS DSA100 optical contact angle measuring device.

DSC measurements were performed at atmospheric pressure by using a TA-Q20 instrument. The weight of sample was around 5 mg. The melting behaviors of the PDLA/PLLA/CNCs blends were investigated through a heating scan with a heating rate of 10^{o}C/min from 40 to 240°C at N_2 atmosphere. The relative stereocomplex formation efficiency (f_{sc}) and crystallinity of the stereocomplex crystals (X_{sc}) in the blends were calculated by means of the following equations [2-5]:

$$f_{sc} = \frac{\Delta H_{m2}}{\Delta H_{m1} + \Delta H_{m2} - \Delta H_{cc}} \quad (1)$$

$$X_{sc} = \frac{\Delta H_{m2}}{\Delta H_{m2}^{o} \times \varphi} \times 100\% \quad (2)$$

where ΔH_{cc} is the exothermic enthalpy of the cold crystallization peak, ΔH_{m1} and ΔH_{m2} are the melting enthalpy of the homocrystallites and stereocomplex crystals, respectively, φ is the weight ratio of PLLA and PDLA in the blends, and ΔH_{m2}^{o}, assumed to be 142J/g, is the melting enthalpy of the ideal stereocomplex crystal [3, 4].

The pressure crystallized PDLA/PLLA/CNCs samples were further cut into small pieces, with the average weight of 0.4g, and placed in the closed test tubes containing 30 mL of hydrolysis media for the evaluation of their hydrolytic degradation performance. To investigate the effect of PH, the hydrolysis experiments were carried out in hydrochloric acid based aqueous solution, distilled water and sodium hydroxide based aqueous solution at the original PH values of 1, 7 and 12, respectively. The PH of the hydrolysis media were monitored, and maintained constant through the periodical medium renewal. For each

sample, the hydrolysis was conducted in the hydrolytic media with different pH values at 58^{o}C for 24 days. Every two days, it was removed from the hydrolytic media, washed with distilled water, and then placed in a vacuum oven at 50^{o}C for 48 h to evaporate the residual moisture. Subsequently, the sample was weighed, and the mass change was recorded. The residual weight fraction (Φ) is calculated as follows [6]:

$$\phi = \frac{W_t}{W_o} \times 100\% \quad (3)$$

where W_t is the residual mass after hydrolysis of the sample, and W_o is its initial mass.

Table S1. DSC data of $PLLA_{49.5}/PDLA_{49.5}/CNCs_1$ blend, crystallized at 200MPa, different temperature for 4h.

Conditions (°C)	T_{cc} [a] (°C)	ΔH_{cc} [a] (J/g)	T_m (hc) [b] (°C)	ΔH_{m1} [b] (J/g)	T_m (sc) [c] (°C)	ΔH_{m2} [c] (J/g)	f_{sc} [d] (%)	X_{sc} [d] (%)
140	-	-	159.5, 178.2	7.3	211.6, 221.9	30.6	80.8	21.8
160	-	-	126.3, 165.5, 178.2	7.5	205.3, 218.3	32.9	81.5	23.4
180	-	-	169.4, 180.3	8.1	211.8, 224.2	35.8	81.6	25.4
200	92.6	2.4	147.9, 174.8	6.4	212.9, 223.9	36.9	90.1	26.3
220	92.4	1.9	172.5	5.4	217.0	46.8	93.1	33.3

[a] T_{cc} is the cold crystallization temperature, and ΔH_{cc} is the exothermic enthalpy of the cold crystallization peak. [b] T_m(hc) and ΔH_{m1} are, respectively, the melting point and melting enthalpy of the homocrystallites. [c] T_m(sc) and ΔH_{m2} are the corresponding melting point and melting enthalpy of the stereocomplex crystals, respectively. [d] f_{sc} is the relative stereocomplex formation efficiency, and X_{sc} is the crystallinity of the stereocomplex crystals.

Table S2. DSC data of $PLLA_{49.5}/PDLA_{49.5}/CNCs_1$ blend, crystallized at different pressure, 220°C for 4h.

Conditions (MPa)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (hc) (°C)	ΔH_{m1} (J/g)	T_m (sc) (°C)	ΔH_{m2} (J/g)	f_{sc} (%)	X_{sc} (%)
0.1	-	-	145.1, 172.4, 178.2	17.4	206.7, 224.7	21.5	55.2	15.3
200	92.4	1.9	172.5	5.4	217.0	46.8	93.1	33.3
300	93.6	4.5	150.0, 174.8	7.6	212.4, 216.3, 223.1	41.2	93.1	29.3
400	89.8	6.6	145.9, 172.9	10.4	214.9	39.4	91.3	28.0
500	92.1	5.4	147.4, 174.8	9.4	214.8, 223.8	35.5	89.9	25.3

Table S3. DSC data of $PLLA_{49.5}/PDLA_{49.5}/CNCs_1$ blend, crystallized at 200MPa, 220°C for different times.

Conditions (h)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (hc) (°C)	ΔH_{m1} (J/g)	T_m (sc) (°C)	ΔH_{m2} (J/g)	f_{sc} (%)	X_{sc} (%)
1	93.1	3.6	150.1, 172.9	7.8	216.2, 223.9	37.3	89.9	26.5
2	95.1	3.5	150.7, 176.4	7.9	216.7, 222.9	42.6	90.5	30.3
4	92.4	1.9	172.5	5.4	217.0	46.8	93.1	33.3
6	96.0	3.4	150.1, 172.9	8.8	216.2, 223.9	43.4	89.0	30.9

Table S4. DSC data of $PLLA_x/PDLA_y/CNCs_z$ blends with various compounding ratios, crystallized at 200MPa, 220°C for 4h.

Conditions (x/y/z)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (hc) (°C)	ΔH_{m1} (J/g)	T_m (sc) (°C)	ΔH_{m2} (J/g)	f_{sc} (%)	X_{sc} (%)
50/50/0	-	-	153.7, 176.9	5.8	217.6	40.1	87.5	28.3
49.5/49.5/1	92.4	1.9	172.5	5.4	217.0	46.8	93.1	33.3
49/49/2	97.7	1.3	174.3	9.2	218.5, 223.3	54.8	87.5	39.4
47.5/47.5/5	88.5	1.1	169.5	5.6	217.3, 224.5	52.7	92.1	39.1

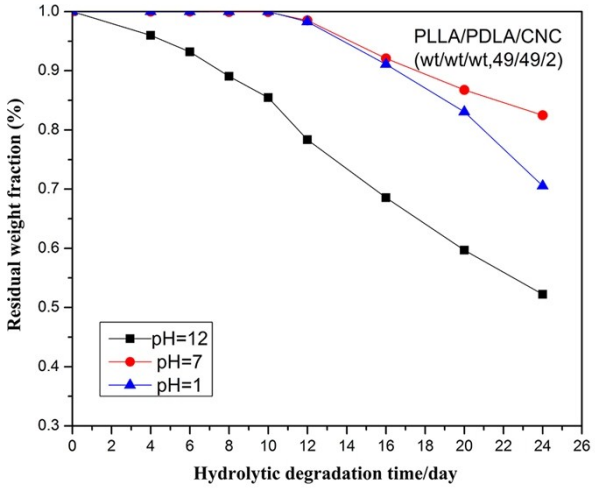

Fig. S1. A comparison for the residual weight fraction changes of $PDLA_{49}/PLLA_{49}/CNCs_2$ during the hydrolysis at PH 1, 7 and 12 in acid, neutral and alkaline media, respectively.

References

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