Supporting Information

Construction of stereocomplex granular dams in sparkling biopolymer systems

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High-Pressure Experiments and Characterization

Experimental procedure of pressure crystallized PLAs/CQDs composites

The pressure and temperature for the crystallization of PLAs/CQDs composites are given based on the P-T phase diagram of PLA by Rohindra et al [1]. The following procedure was used for pressure crystallization. After loading the PLAs/CQDs samples, the temperature was increased to a level and maintained for 10 min to allow the fully melting of the polymers. Subsequently, the temperature and pressure were raised to the predetermined level. The samples were kept under these conditions for a predetermined time, and then quenched to ambient conditions. This procedure ensured the minimum degradation of PLAs at elevated temperature, and they would be in a molten state before polymer crystallization occurred [1-3].

Characterization

TEM observations were performed using a JEOL JEM-2100F device. LSCM detections were conducted with a KEYENCE VK-9700 apparatus. WAXD results were obtained at room temperature with a PANalytical X'pert PRO diffractometer using a Cu Kα radiation source in the scanning angle range of 2θ = 5°−50° at a scan speed of 10°/min. After etching by a configured solution, the sample surfaces were coated with gold for SEM observations using a JSM-6330F apparatus.

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 PLAs/CQDs 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 [2-6]:

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

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

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 [2-6].

The hydrolysis experiments of PLAs/CQDs samples were carried out at the original pH values of 1, 7 and 12 in closed test tubes containing hydrochloric acid based aqueous solution, distilled water and sodium hydroxide based aqueous solution, respectively. The pH values of the hydrolytic media were monitored and kept constant through regular media updates. The hydrolysis was conducted at 58^{o}C for each sample. The samples were removed from the hydrolytic media every few days, washed with distilled water, and then placed in a vacuum oven to evaporate the residual moisture. Following that, they were weighed, and

their mass changes were recorded. The residual weight fraction (Φ) is calculated as follows [2, 3, 7]:

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

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

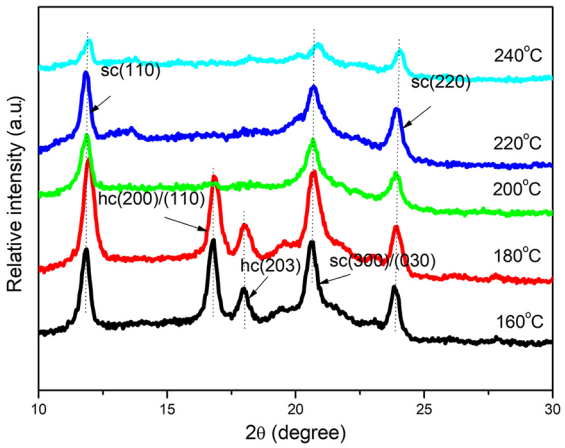

Fig. S1. WAXD profiles of $PDLA_{49.5}/PLLA_{49.5}/CQDs_1$ blend, crystallized at 200MPa and different temperatures for 4h.

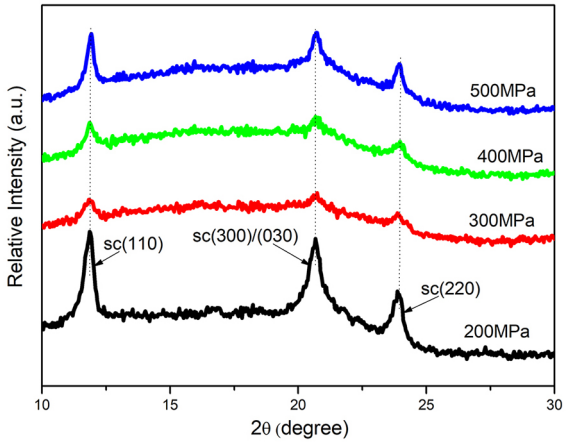

Fig. S2. WAXD profiles of $PDLA_{49.5}/PLLA_{49.5}/CQDs_1$ blend, crystallized at different pressures and 200°C for 4h.

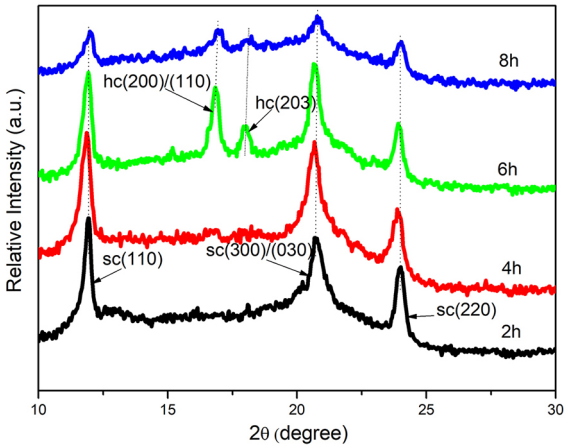

Fig. S3. WAXD profiles of $PDLA_{49.5}/PLLA_{49.5}/CQDs_1$ blend, crystallized at 200MPa and 200°C for different times.

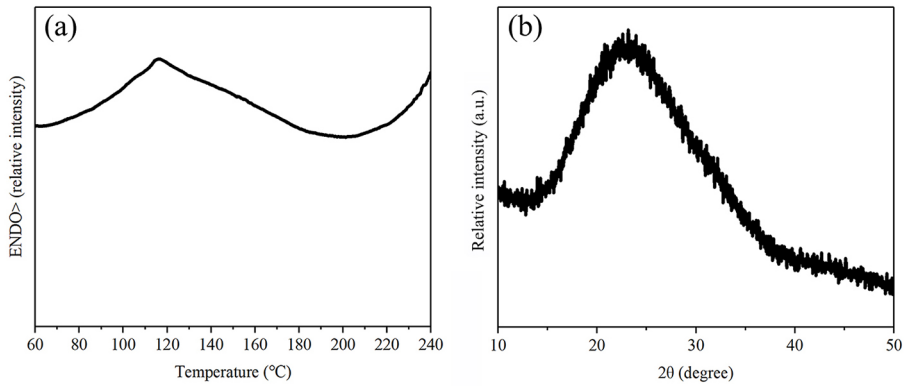

Fig. S4. DSC (a) and WAXD (b) measurements of original CQDs. In the DSC thermogram, the broad endothermal peak that centers at 116.6°C is associated to the dehydration of CQDs [8, 9]. For the WAXD pattern, it exhibits a wide diffraction peak at 22.9°, corresponding to the plane (002) of CQDs [10, 11].

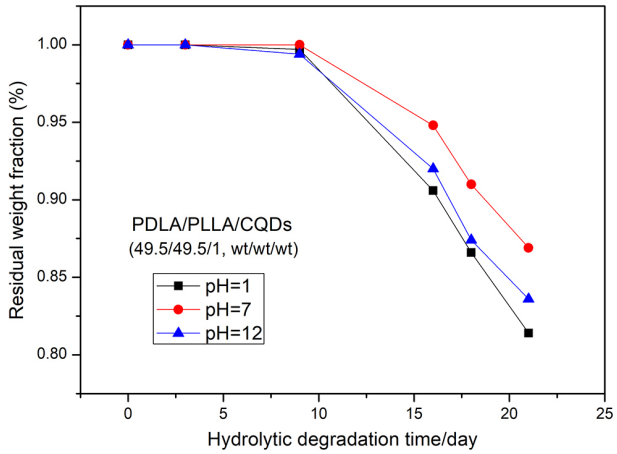

Fig. S5. A comparison for the residual weight fraction changes of $PDLA_{49.5}/PLLA_{49.5}/CQDs_1$ during the hydrolysis at pH 1, 7 and 12 in acid, neutral and alkaline media, respectively.

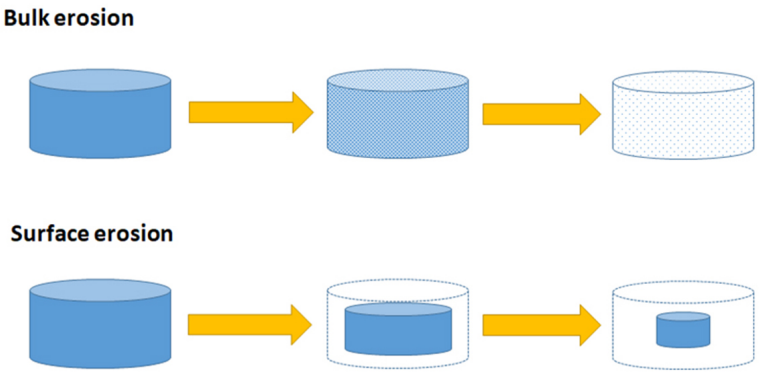

Fig. S6. Schematic illustration of the mechanisms of bulk erosion (top) and surface erosion (bottom) in the hydrolytic degradation of PLAs/CQDs blend samples.

References

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