Novel biobased poly(hexamethylene-*co*-diethylene glycol furandicarboxylate) copolyesters with improved mechanical property and hydrolytic degradation rate

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Materials

Hexanediol (HDO, 99.5%) was purchased from Shanghai Macklin Biochemical Co., Ltd. Dimethyl furandicarboxylate (DMFD, 99%) was obtained from Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences. DEG was acquired from Xilong Science. The catalyst tetrabutyl titanate (TBT, 99%) was obtained from Beijing Changping Jingxiang Chemical Reagent Factory. Without further purification, they were directly used as received.

Synthesis of PHF, PDEGF, and PHDEGF

PHDEGF copolyesters were prepared by a two-step melt polycondensation method. Firstly, DMFD, DEG, and HDO were put into a 250 mL three-necked flask in the ratio of DMFD:(HDO+DEG) = 1:1.2, and 1 mL of TBT at a concentration of 0.1 g/mL was added. The reaction was kept under nitrogen atmosphere for 15 min with the mechanical stirring rate at 200-300 r/min. In the transesterification stage, the reaction was carried out by firstly increasing the temperature to 180 ^{o}C for 2 h, followed by increasing the temperature to 220 ^{o}C for 2 h until no methanol was evaporated. In the polycondensation stage, the vacuum device was replaced. The pressure of the device was first lowered to about 1000 Pa for 0.5 h. Subsequently, the pressure was further slowly lowered to 200 Pa within 0.5 h. The reaction continued for about 3 h at 230 ^{o}C under about 100-200 Pa until the rod climbing phenomenon occurred. PHF and PDEGF were similarly prepared as above.

The appearance of all the samples after molding is illustrated in Figure S1. The color of the PHDEGF copolyester showed yellow and brown, which was typical of furan-based polyesters.

Figure S1. Appearance of PHF, PDEGF, and PHDEGF samples.

Characterizations

The composition and chemical structures of PHF, PDEGF, and PHDEGF were confirmed by ^{1}H Nuclear magnetic resonance (^{1}H NMR) and ^{13}C Nuclear magnetic resonance (^{13}C NMR) on a Bruke AV 600 spectrometer at room temperature. Deuterated chloroform ($CDCl_3$) was used as the solvent.

The intrinsic viscosity ([η]) values were measured at 25 ^{o}C by an Ubbelohde viscometer in a phenol/1,1,2,2-tetrachloroethane (3/2, w/w) mixed solvent.

The thermal stability was studied under nitrogen atmosphere with a TA Q50 thermogravimetric analysis (TGA) at a heating rate of 20 ^{o}C/min.

The thermal behavior tests were carried out on a TA Q100 differential scanning calorimeter (DSC) under nitrogen atmosphere. For the glass transition temperature study, the experimental steps were as follows. After eliminating the thermal history, the samples were cooled to −50 ^{o}C at 60 ^{o}C/min and then heated to 180 ^{o}C at 10 ^{o}C/min. For the melt crystallization behavior study, a cooling rate of 10 ^{o}C/min was used after the thermal history of the samples was completely erased. The samples were subsequently heated to180 ^{o}C at 10 ^{o}C/min.

The crystal structure study was performed on a Rigaku Ultima IV X-ray diffractometer from 5^{o} to 50^{o} at 5^{o}/min. PHF and PHDEGF10 were crystallized at 110 ^{o}C for 10 h, PHDEGF30 were crystallized at 80 ^{o}C for 10 h. From PHDEGF50 to PDEGF, all polyesters were isothermally crystallized at 50 ^{o}C for 10 h.

The tensile properties were measured at room temperature with a tensile rate of 20 mm/min on a universal tensile testing machine (UTM5205XHD) after the samples were hot-pressed and cut into dumbbell shape. The data were obtained from the average values of at least 3 tests.

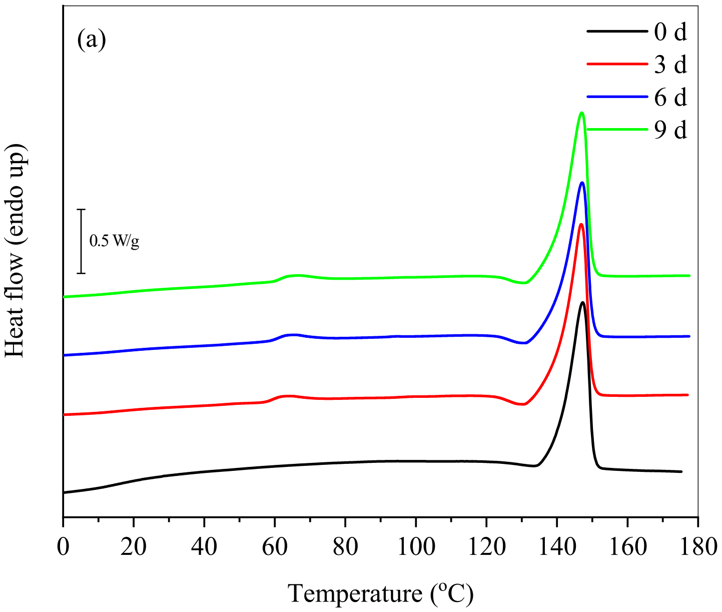
The instrument used for the water contact angle test was the OCA 50AF contact angle tester. The data were the average of the results obtained by at least three tests.

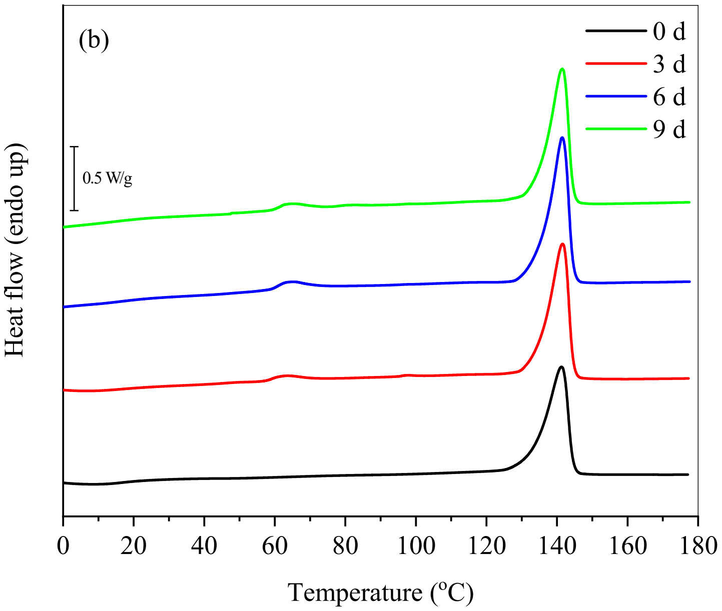
The samples in size (10 mm×10 mm×1 mm) were placed in vials containing NaOH solution with pH=14 in a constant temperature water oscillator for degradation at a speed of 200 r/min and a temperature of 37 ^{o}C. The samples were removed at certain days, rinsed with deionized water, and dried. The mass loss was calculated by the following equation.

$$W_{\text{loss}} = \frac{W_0 - W_1}{W_0}$$

where W_0 was the initial mass of the sample and W_1 was the mass of the degraded sample.

A scanning electron microscope (SEM) (JEOL, JSM-7800) was used to observe the surface of degraded polyesters. Before observation, the surfaces of all samples were coated with gold.


(a)
0 d
3 d
6 d
9 d
0.5 W/g
Heat flow (endo up)
0
20
40
60
80
100
120
140
160
180
Temperature (°C)


(b)
0 d
3 d
6 d
9 d
0.5 W/g
Heat flow (endo up)
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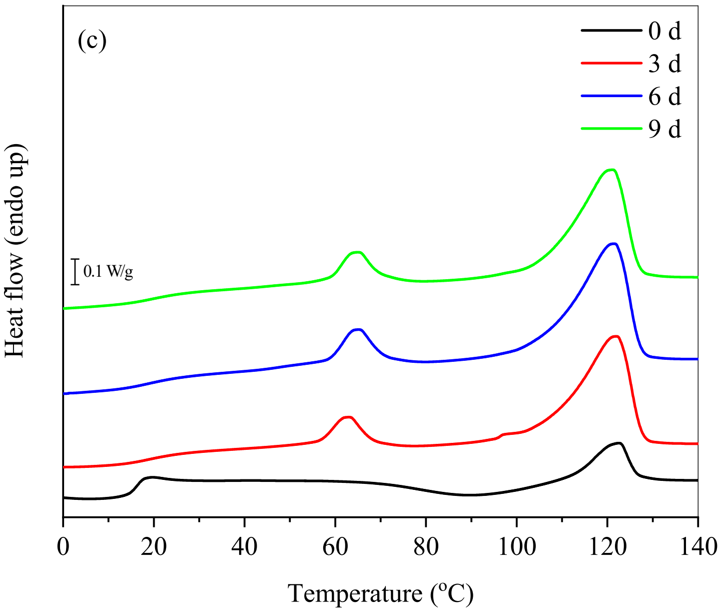
20
40
60
80
100
120
140
160
180
Temperature (°C)


(c)
0 d
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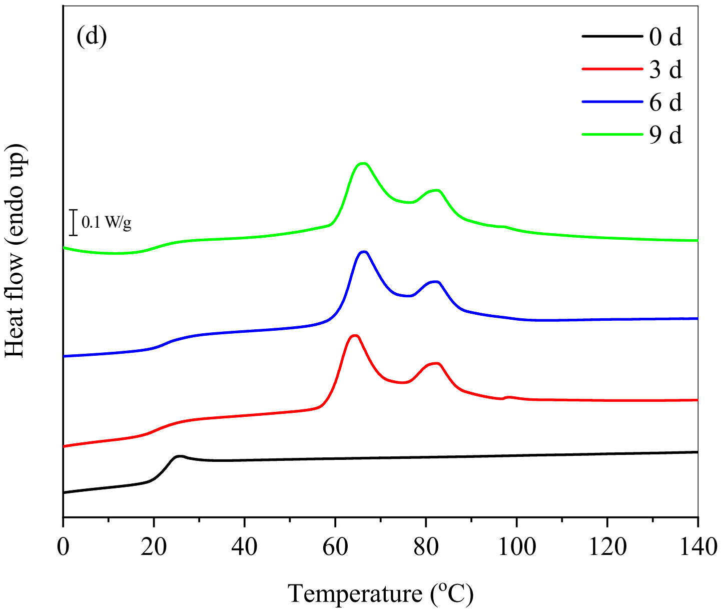
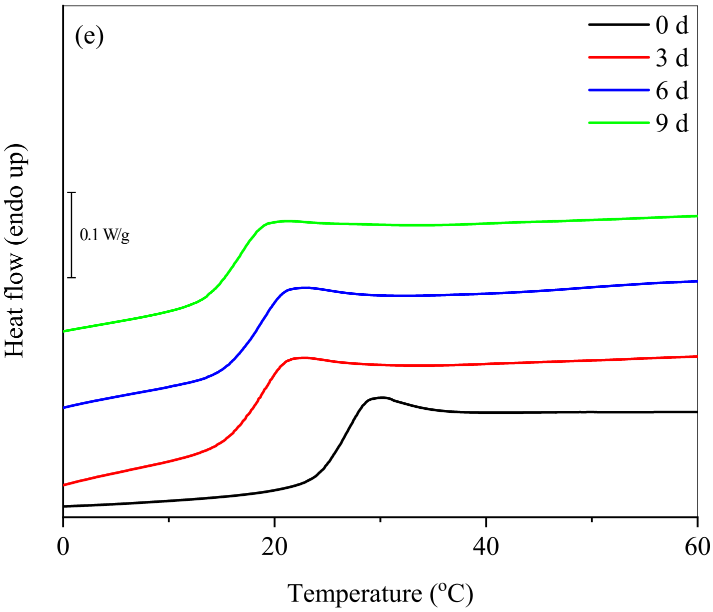
6 d
9 d
0.1 W/g
Heat flow (endo up)
0
20
40
60
80
100
120
140
Temperature (°C)


(d)
0 d
3 d
6 d
9 d
0.1 W/g
Heat flow (endo up)
0
20
40
60
80
100
120
140
Temperature (°C)


(e)
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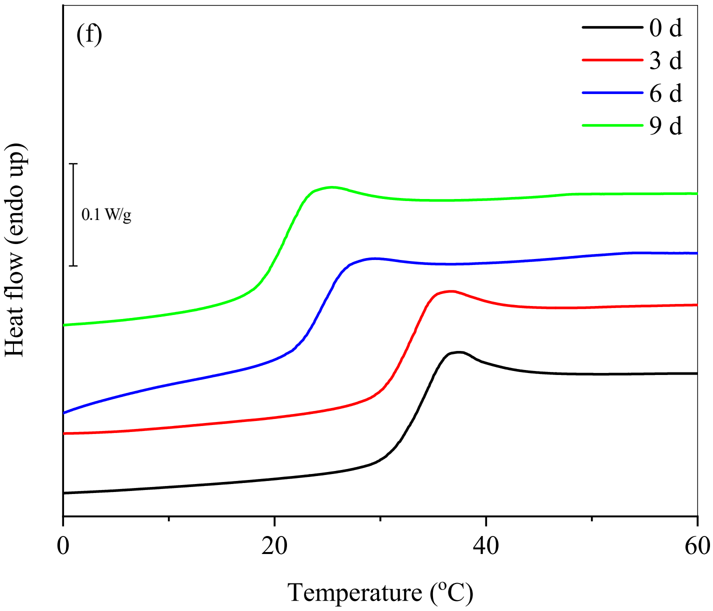
6 d
9 d
0.1 W/g
Heat flow (endo up)
0
20
40
60
Temperature (°C)


(f)
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6 d
9 d
0.1 W/g
Heat flow (endo up)
0
20
40
60
Temperature (°C)

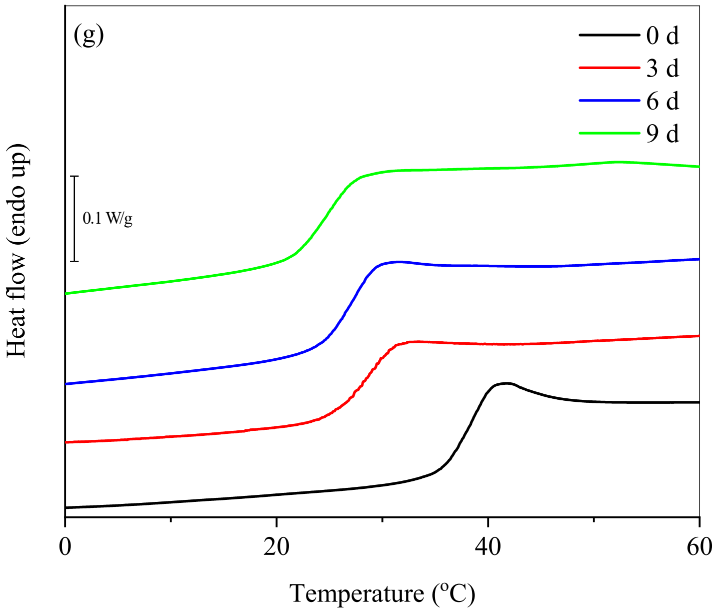

Figure S2. DSC scans of (a) PHF, (b) PHDEGF10, (c) PHDEGF30, (d) PHDEGF50, (e) PHDEGF70, (f) PHDEGF90, and (g) PDEGF after hydrolytic degradation for different times.

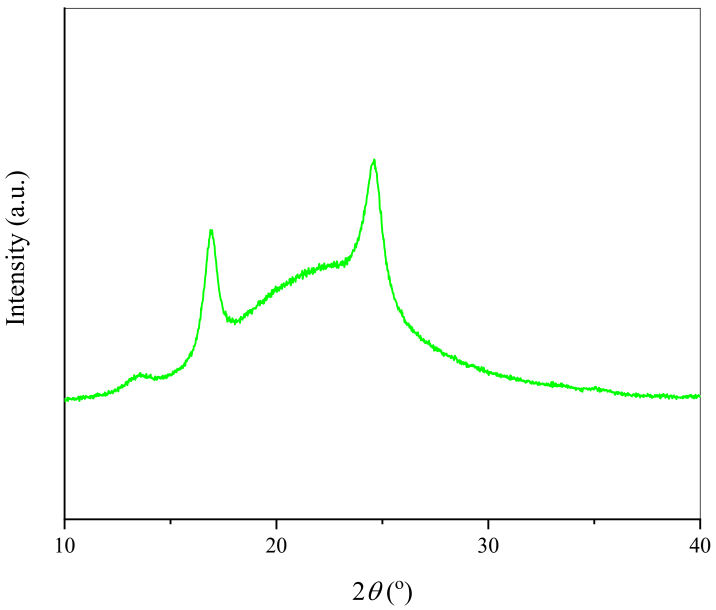

Figure S3. WAXD profile of PHDEGF50 after a hydrolytic degradation of 3 d in NaOH (pH=14, 37 °C).