Experimental and Theoretical Study on Glycolic Acid Provided Fast

Bio/Seawater Degradable Poly(Butylene Succinate-co-Glycolate)

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Characterization Methods of PBSGAs.

Intrinsic viscosity was tested by a Ubbelohde viscometer (inner diameter 0.792 mm) at 25 °C, with 125 mg of sample dissolved in 25 mL solvent of phenol/1,1,2,2-tetrachloroethane (50/50, w/w).

Determination of molecular weight (M_w) and distribution (DI) were carried out using a GPC (Agilent PL-GPC220) at 40 °C, with 10 mg of sample dissolved in 10 mL of chloroform. Chloroform was used as the mobile phase at the flowing rate of 1 mL/min. M_n and DI were determined using polystyrene standards (3070-258000 g/mol).

The chemical compositions were confirmed by ¹H NMR, which were recorded on a Bruker AVIII400 NMR spectrometer at 25 °C with deuterated chloroform as solvent. The composition (n_{GA}), the number-average sequence length of GA and BS units (L_{GA} , L_{BS}) and the degree of randomness (R) were calculated from ¹H NMR data.

FT-IR spectra were obtained using an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) (Agilent Cary 600 Series FT-IR) spectrometer. The scan range was from 500 cm^{-1} to 4000 cm^{-1} and each sample was scanned for 32 times.

The thermal transitions were recorded with DSC (Diamond DSC, PerkinElmer) under N₂ flow of 40 mL min⁻¹. The sample was firstly heated from -40 to 200 °C with 10 °C /min ramp, and then the temperature was kept at 200 °C for 3 min. Then, it was subsequently cooled to -40 °C and hold for 3 min. Finally, the second heating run was performed by heating the sample to 200 °C at 10 °C /min too. The melting temperature (T_m) and corresponding entropy (ΔH_m), glass transition temperature (T_g), cold crystallization temperature (T_{cc}) and its entropy (ΔH_{cc}) were obtained.

The thermal stability was determined by TGA experiment (Mettler-Toledo TGA/DSC) in dry N₂ atmosphere (50 mL/min). The samples around 5-8 mg were heated to 800 °C with the heating rate of 20 °C/min. The temperature at 5% weight loss (T_{d,5%}) and the temperature at the maximum rate (T_{d,max}) were summarized.

The patterns of X-ray diffraction were obtained with Bruker AXS D8 Advance, using Cu-K α radiation (λ =0.1541 nm) in the range from 5 to 60° at the rate of 5°/min. The PBSGA samples for XRD tests were stored at room temperature for 2 weeks.

All samples for mechanical tests and barrier tests were prepared by compression molding and cold pressing, and then conditioned at room temperature for 2 weeks before testing.

Tensile properties were obtained at 25 °C by an Instron 5567, according to ASTM D638. The crosshead speed was 20 mm/min and the gauge length was 15 mm. Dumbbell-shaped specimens (1×2 mm in neck thickness and width) were prepared.

Surface hydrophobicity values of films were determined based on measurement of the water contact angle and seawater contact angle using a WCA analyzer OCA20 (Data physics Ltd., Germany) at normal room temperature and pressure. Five drops were observed on different areas for each film and contact angles were reported as the average value \pm standard deviation.

The CO₂ and O₂ barrier properties of PBSGAs were performed at 23 °C by using Labthink VAC-V2. The films with surface area of 38.5 cm² were prepared by meltpress. The water barrier properties of samples (33 cm²) were studied at 38 °C and 90% RH by Labthink W3-060.

Enzymatic degradation experiments of PBSGAs films (0.3-0.35 mm in thickness) were carried out in Phosphate Buffered Saline (pH 7.4) at 37 °C, catalyzed by 0.1 mg/mL of Candida antarctica lipase B (CALB) enzymes. Meanwhile, a controlled experiment was run parallel with them in distilled water. In the marine degradation tests, the PBSGA films were added into artificial seawater at 10-15 °C. After 7 d intervals, the films were washed with distilled water, and dried under vacuum at 40 °C to constant weight. The media was replaced every 7 days to ensure a stable degradation. The degradation level was evaluated by the weight percentage of residue, according to the following equation (S1):

Residue Weight (%) =
$$\frac{w_t}{w_0} \times 100\%$$
 (1)

Where W_0 is the original weight, and W_t is the weight after degradation.

Storage stability tests of PBSGAs films were performed at room temperature with 70% RH. After every month of storage, recorded the intrinsic viscosity of copolyesters.

Theoretical Calculation Method

In order to obtain all stable configurations on the potential energy surface of the 3-1 complex and 5-1 complex, 100 initial complexes were randomly generated by the genmer in the cluster configuration search program Molclus¹ without relying on empirical judgments. The geometry optimization and frequency analysis of these structures were performed using the extended tight-binding semiempirical program package (xTB); the geometries and energies were obtained with GFN2-xTB.²⁻³ These initial geometries in a rough level conformation with relatively low energy and different geometry were screened out the isostat tool in Molclus to sort count the energy of the complexes and remove the repetitive structures with similar energy and high geometric similarity. The parameter settings used the default values in the program, i.e., the energy threshold for distinguishing clusters, 0.5 kcal/mol, and the geometric threshold for distinguishing clusters, 0.25 Å. Finally, the optimized isomers were sorted in energy, and the 10 lowest-lying ones were treated with Gaussian 16 software to obtain the precise geometries at a level of $B3LYP/6-31G(d,p)^4$ with Grimme D3 dispersion.⁵ The prediction of reactive sites between nucleophile and electrophile was studied by the frontier molecular orbital (FMO) analysis and with hirshfeld charges ⁶ and with Fukui functions (FF). The Fukui function was used to predict reactive sites at the B3LYP-D3/def-TZVP level of theory. Fukui function is defined as ⁷⁻⁸:

$$= \left[\frac{\partial \rho(r)}{\partial N}\right]_{v}$$
(2)

where N is number of electrons in present system, the constant term in the partial derivative is external potential. For a given molecular system, Fukui function was calculated using electron density of three states:

$$f^{+}(r) = \rho_{N+1}(r) - \rho_{N}(r) \approx \rho^{LUMO}(r)$$
 (3)

$$f^{-}(r) = \rho_{N}(r) - \rho_{N-1}(r) \approx \rho^{HOMO}(r)$$
 (4)

$$f^{0}(r) = \frac{f^{+}(r) + f^{-}(r)}{2} = \frac{\rho_{N+1}(r) - \rho_{N-1}(r)}{2}$$
$$\approx \frac{\rho^{HOMO}(r) + \rho^{LUMO}(r)}{2}$$
(5)

where N is the number of electrons in the current molecular system. The N - 1 and N + 1 states share the same molecular geometry as the N state. For nucleophiles, f^- is the reactivity descriptor, while for electrophiles, f^+ is the descriptor. f^0 is reactivity descriptor for radical attack. Atoms with larger Fukui function tend to have higher reactivities. Molecular polarity index (MPI) was also calculated, for which is expressed as:

$$MPI = (1/A) \iint_{S} |V(r)| dS$$
(6)

where A and V(r) refer to the area of vdW surface and value of ESP at a point r in space, respectively. The integration is performed over the whole molecular vdW surface (S). MPI is a quite reliable index of measuring molecular polarity, the larger the index, the higher the polarity.⁹ Isosurface maps were produced using VMD 1.9.3.¹⁰ program based on outputs from the Multiwfn calculations.¹¹

A further frequency calculation at the same level of theory were performed to confirm each stationary point to be either an intermediate or a transition structure after structural optimizations at a level of B3LYP/6-31G (d,p) with Grimme D3 dispersion. In addition, the intrinsic reaction coordinates (IRC) calculations¹² and relaxed potential surface scans were carried out to identify transition states and immediate reactants and products to study the mechanism of hydrolysis. The electronic energies were updated with the single point calculation of the larger basis sets, i.e., B3LYP-D3/6-311+G(d,p).



Figure S1. ATR-FTIR spectra of PBFGAs.



Figure S2. (a) TGA and (b) DTG curves of PBSGAs.



Figure S3. Distilled water and seawater contact angle images of PBSGAs.

Sample	Before degradation		After 49 days of seawater degradation	
	M _w (g/mol)	DI	M _w (g/mol)	DI
PBS	1.18*10 ⁵	2.1	9.88*10 ⁴	2.2
PBSGA5	1.35*10 ⁵	1.9	9.27*10 ⁴	2.3
PBSGA10	$6.24*10^4$	2.0	$4.60*10^4$	2.3
PBSGA20	$8.98*10^4$	2.2	3.26*10 ⁴	2.5
PBSGA25	$7.09*10^4$	2.3	$2.08*10^4$	2.6
PBSGA30	7.73*10 ⁴	2.2	1.35*10 ⁴	2.5
PBSGA40	6.71*10 ⁴	2.1	$4.06*10^3$	2.7

 Table S1. Molecular weight changes of PBSGAs after 49 days of seawater degradation.



Figure S4. 3-1 and **5-1** segment model for Fukui function (FF) analysis. The **3-1** model was close to the segment of PBSGA40 and the **5-1** model was that of PBSGA30, as calculated from the ¹H-NMR data.



Figure S5. Prediction of the active sites by frontier molecular orbital (FMO) theory. Isosurface of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of 3-1 model (A) and 5-1 model (B), respectively. Red and blue isosurfaces represent positive and negative parts, respectively.

Table S2: Comparison of the values of hirshfeld charges and Fukui functions for C1 atom of GA units in the **3-1** model and **5-1** model. The f^+ can be expressed as the difference of atomic charges in two states. The atom owing larger values of f^+ became the favorable sites for nucleophilic attack.

Atom	q(N)	q(N+1)	q(N-1)	f^+
C1(3-1)	0.2161	0.1457	0.2179	0.0704
C1(5-1)	0.2072	0.1610	0.2089	0.0463

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