

Incorporation of 1,4-cyclohexanedicarboxylic acid into poly(butylene terephthalate)-b-poly(tetramethylene glycol) to Alter Thermal Properties without Compromising Tensile and Elastic Properties

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Characterization

Molecular weights and molecular weight distributions were measured on a PL-GPC220 high temperature GPC. HPLC grade chloroform was used as elution solvent at 40°C and molecular weight was calibrated with polystyrene standards. The concentration of all samples was 20mg/3mL.

Structure and compositions of PBCT-PTMG copolymers were determined by proton nuclear magnetic resonance (¹H NMR) in CDCl₃ solvent using a Bruker AVIII400 NMR spectrometer at room temperature.

Tensile testing was performed by using an Instron5567 tensile testing machine with a 500N load cell. The stretching rate was 100mm/min and the test temperature was 25°C. Dumb-bell-shaped sample bars with dimensions of 35.0mm (length), 3.0mm (neck width) and 0.5mm (thickness) were prepared by press-molding at temperature 20°C higher than T_m of the sample and subsequently cooled down to temperature below its T_c without releasing the pressure. All data were obtained by averaging the data from five parallel measurements.

Cyclic tensile testing was done with an Instron 5567 apparatus. The dumb-bell-

shaped sample bars with dimensions of 35.0 mm (length), 3.0 mm (width), and 0.5 mm (thickness) were stretched to a ε_m of 500% elongation at room temperature with a 100 mm/min stretching rate. Then the clamps began to return with a speed of 50 mm/min until the force on the sample was zero. After the above two steps, one cycle was complete. Three samples were tested to calculate mean values and standard deviation. Every sample was subjected to 5 cycles and the shape recovery rate (R_r) was calculated according to the following equation:

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)}$$

where N is the cycle number, ε_m is the maximum strain imposed on the material, $\varepsilon_p(N)$ and $\varepsilon_p(N-1)$ are the strains of the sample in two successive cycles when the force on the sample is 0 and $R_r(N)$ is based on two successive cycles.

DSC measurements were performed using a differential scanning calorimeter (Mettler-Toledo DSC I). Measurements were performed under a nitrogen atmosphere at a flow rate of 50mL/min. About 5mg of sample was placed in an alumina sample pan and the measurement was carried out according to the following process: the sample was heated up to 260°C at 10 K/min and held at this temperature for 4min to erase the heat history. It was then cooled down to 40°C at 10K/min. Subsequently, a second heating scan was performed at 10K/min to 260°C. The melting point (T_m) and heat of fusion (ΔH_m) were obtained from the second heating scan and the crystallization temperature (T_c) was taken from the cooling scan. The degree of crystallinity of the hard segment was calculated according to the following equation:

$$\chi_c(\%) = \frac{\Delta H_m}{f(\text{PBT}) \times \Delta H_m^\theta(\text{PBT}) + f(\text{trans-PBC}) \times \Delta H_m^\theta(\text{trans-PBC})} \times 100\%$$

where χ_c is the percentage of crystallinity of the hard segment, f is the weight fraction, ΔH_m is the experimental melting heat of fusion, and ΔH_m^θ is the heat of fusion of 100% crystalline (140J/g for PBT and 141J/g for *trans*-PBC calculated according to the group contribution theory).^{1,2}

Thermal stability measurements were conducted using a TGA instrument (Mettler-Toledo TGA/DSC thermogravimetric analysis). For each sample, 6–10 mg sample was placed in a ceramic furnace and the TGA curve was recorded ranging from 50°C to 800°C with a heating rate of 10 K/min under dry air atmosphere with a flow rate of 50mL/min. We took the temperature at which the weight loss was 5% ($T_{5\%}$) as an index to evaluate the thermal stability of the sample.

Composition of PBCT-PTMG copolymer

The composition of the PBCT-PTMG copolymers are calculated based on the integration of these five peaks, I_a , I_b , I_c , I_d and $I_{b'+d'}$ according to equations (S1)-(S5). Furthermore, peaks with chemical shifts at $\delta = 2.47$ (*e-cis*) and 2.27 (*e-trans*) are signals from *cis*- and *trans*-CHDA respectively, and the integration of these two peaks I_{e-cis} and $I_{e-trans}$ can be used to calculate the amount of *trans*-CHDA according to equation (S6).

(S1)

$$\text{PBT Hard wt}\% = \frac{220 \times I_a}{220 \times I_a + (132 + 72 \times \frac{I_{b'+d'}}{I_{b+d}}) \times I_b + 226 \times I_c + (138 + 72 \times \frac{I_{b'+d'}}{I_{b+d}}) \times I_d} \times 100\%$$

(S2)

$$\text{PBT Soft wt}\% = \frac{(132 + 72 \times \frac{I_{b'+d'}}{I_{b+d}}) \times I_b}{220 \times I_a + (132 + 72 \times \frac{I_{b'+d'}}{I_{b+d}}) \times I_b + 226 \times I_c + (138 + 72 \times \frac{I_{b'+d'}}{I_{b+d}}) \times I_d} \times 100\%$$

(S3)

$$\text{PBC Hard wt}\% = \frac{226 \times I_c}{220 \times I_a + (132 + 72 \times \frac{I_{b'+d'}}{I_{b+d}}) \times I_b + 226 \times I_c + (138 + 72 \times \frac{I_{b'+d'}}{I_{b+d}}) \times I_d} \times 100\%$$

(S4)

$$\text{PBC Soft wt}\% = \frac{(138 + 72 \times \frac{I_{b'+d'}}{I_{b+d}}) \times I_d}{220 \times I_a + (132 + 72 \times \frac{I_{b'+d'}}{I_{b+d}}) \times I_b + 226 \times I_c + (138 + 72 \times \frac{I_{b'+d'}}{I_{b+d}}) \times I_d} \times 100\%$$

(S5)

$$\text{CHDA mol}\% = \frac{I_c + I_d}{I_a + I_b + I_c + I_d} \times 100\%$$

(S6)

$$\text{trans-CHDA mol}\% = \frac{I_{e-trans}}{I_{e-cis} + I_{e-trans}} \times 100\%$$

References:

- (1) K. G. Joback, R. C. Reid, *Chem. Eng. Commun.*, 1987, **57**, 233–243.
- (2) Y. H. Park, C. G. Cho, *J. Appl. Polym. Sci.*, 2001, **79**, 2067–2075.