



# Modifying poly(ethylene terephthalate) for low-density foams

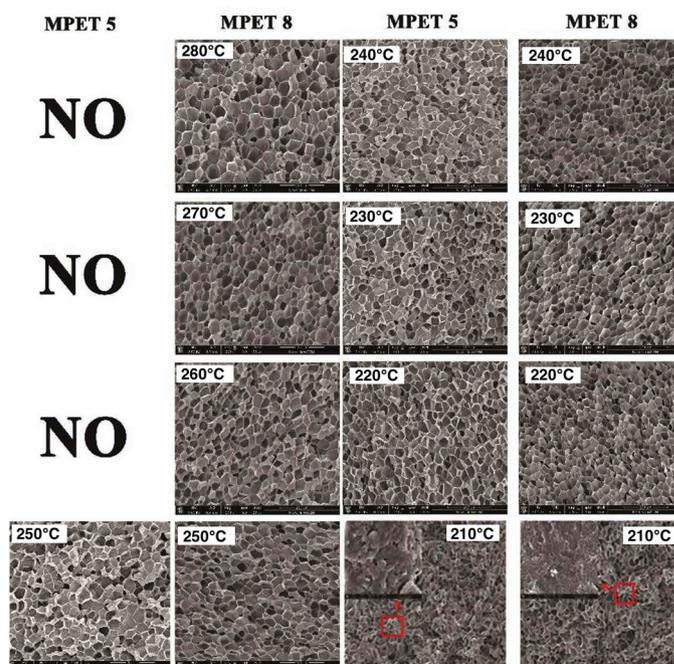
Ling Zhao, Tian Xia, Zhenhao Xi, Tao Liu, Xun Pan, and Chaoyang Fan

*Reactive extrusion with pyromellitic dianhydride and controlled foaming of the melt with supercritical carbon dioxide produce high-melt-strength poly(ethylene terephthalate) foam.*

Poly(ethylene terephthalate) (PET) foams, which show good mechanical properties and high temperature dimensional stability, are used in packaging, thermal insulating, and construction applications.<sup>1,2</sup> However, commercial PET with a linear molecular chain usually has low molecular weight, melt elasticity, and melt strength. As a consequence of the low melt strength, it cannot resist intense deformation of cells during foaming: the cells collapse and coalesce, and the foam has either open cells or no cells. We tried to controllably prepare closed cells and a foam suitable for structural materials, insulated panels, and core components for sandwich structures.

In the past, attempts to improve the melt strength of PET have included in-situ modification<sup>3</sup> or reactive extrusion.<sup>2</sup> Reactive extrusion has the twin advantages of lower costs and simple preparation using standard industrial extruders operated at normal conditions and is, therefore, more attractive. It is well known that a high molecular weight, broad molecular weight distribution, and a long chain branch attached to the polymer backbone improve the polymer melt strength by enhancing entanglement in the polymeric melt. Modifying agents that have electrophilic functional groups, such as cyclic anhydride, react with the nucleophilic end groups of PET within the residence time limits of extruders.<sup>2,4</sup> Pyromellitic dianhydride (PMDA) is frequently used to modify PET for higher melt strength. It has a melting point close to the PET processing temperature, and this—together with a relatively high number (four) of functional groups per molecule, and so a high concentration of reactants—ensures fast reactions between PMDA and PET.

Supercritical carbon dioxide (scCO<sub>2</sub>), an environmentally friendly blowing agent for polymer foaming, changes the polymer's physical properties and enables manipulation of the foaming process.

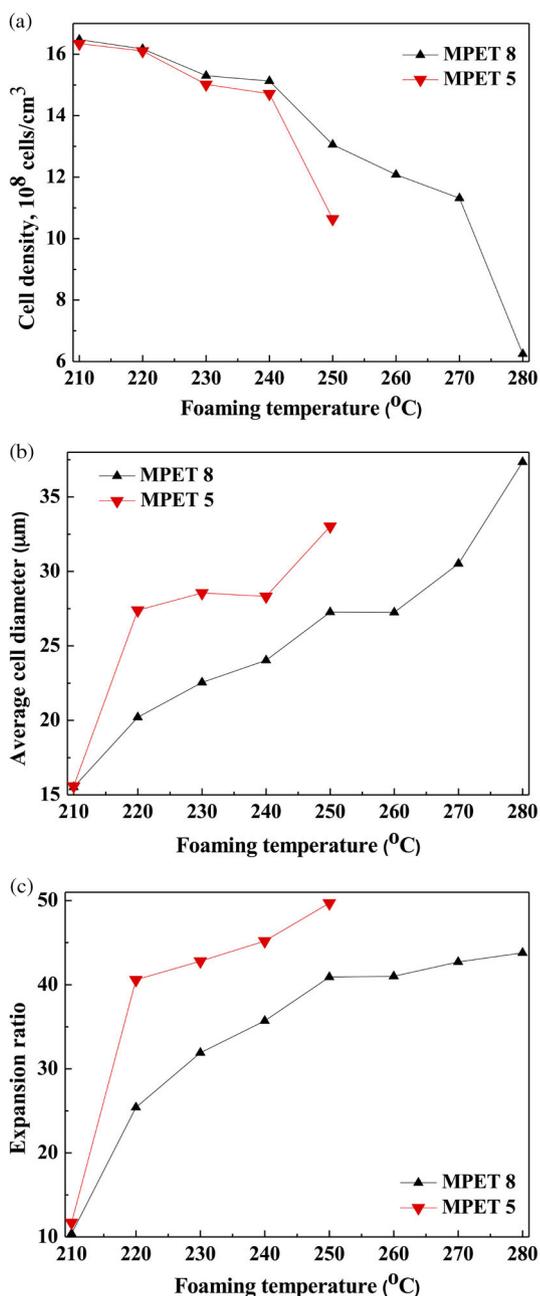


**Figure 1.** Cell morphology of foams prepared at different foaming temperatures from poly(ethylene terephthalate) (PET) modified with pyromellitic dianhydride (PMDA). MPET 5, MPET 8: Composites containing 0.5 and 0.8% by weight PMDA, respectively.

Modified PET foam has been produced by extrusion foaming using scCO<sub>2</sub>; Xanthos and colleagues have reported a cell diameter of 270–350 μm and an expansion ratio of 3–7.<sup>5</sup> Here, we combine these two techniques to obtain PET foams with higher expansion ratios (10–50) and smaller cells (15–37 μm).<sup>6</sup> We modified PET by reactive extrusion with PMDA and used scCO<sub>2</sub> as the blowing agent in a batch foaming process.

As a proxy for molecular weight, we measured the intrinsic viscosity (IV) against reaction temperature (T<sub>E</sub>) of PMDA-modified PET. At

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**Figure 2.** Characterization of MPET foams obtained at different foaming temperatures. (a) Cell density, (b) average cell diameter, and (c) expansion ratio.

first, IV increased with  $T_E$ , reaching a maximum when  $T_E$  was close to the melting point of PMDA. IV then decreased as  $T_E$  continued to increase, indicating that the degradation reaction started to dominate. IV monotonically increased with residence time with PMDA content

of 0.5 and 0.8% by weight. As expected, IV initially increased with PMDA content. However, we observed the opposite trend for PMDA content higher than 0.8% by weight, when the main reaction between PET and PMDA changed to an end-capping reaction.

We characterized PET modified with different PMDA content by dynamic shear rheology. The melt elasticity and strength of PET were improved by the reactive extrusion process, and increased with PMDA content. We used an extended Avrami analysis for non-isothermal crystallization of modified PETs.<sup>7</sup> Introducing a long chain branch to the backbone of PET accelerated the non-isothermal crystallization under atmospheric nitrogen and high-pressure CO<sub>2</sub> across the experimental range of degrees of branching, which hindered cell growth and solidified the cell structure more rapidly by stiffening the polymer matrix.

In the foaming process, we loaded an autoclave with PET and heated it to 280°C at 20MPa for 20min. Afterwards, the autoclave was cooled to the foaming temperature, re-pressurized to 20MPa, and kept at the foaming condition for another 10min. We then quenched the pressure to the ambient pressure via a maximum depressurization rate of 330MPa/s. Figure 1 shows the cell morphologies of the PET foams we obtained at different temperatures (210–280°C for MPET 8 and 210–250°C for MPET 5; MPET 5 and MPET 8 were PETs modified with 0.5 and 0.8% by weight PMDA, respectively). Compared with MPET 8 foam, MPET 5 foam had a lower melt strength, resulting in bigger cells, a higher expansion ratio, and lower cell density. The cell size and expansion ratio increased, and the cell density decreased with the foaming temperature: see Figure 2. The maximum foaming temperature depended on the melt strength, which decreases with foaming temperature. The lowest foaming temperature was the crystallization temperature.

In summary, we modified PET by reactive extrusion with PMDA to obtain a high melt strength and non-isothermal crystallization rate. We also obtained broad foaming temperature windows for batch foaming with scCO<sub>2</sub>. We controllably produced PET foam with cell diameter 15–37μm, cell density 0.6–1.6×10<sup>9</sup> cells/cm<sup>3</sup>, and an expansion ratio of 10–50. We are now designing an integrated process of melt modification and foaming of PET using scCO<sub>2</sub>. The extrudates of reactive extrusion are pumped into a falling film column charged with high-pressure CO<sub>2</sub>, in which the modifying reactions between PET and PMDA and the saturation stage of the foaming process take place simultaneously. Cell nucleation is induced by a pressure drop at a capillary die.

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#### Author Information

Ling Zhao, Tian Xia, Zhenhao Xi, Tao Liu, Xun Pan, and Chaoyang Fan

State Key Laboratory of Chemical Engineering  
East China University of Science & Technology  
Shanghai, China

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