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Supercritical CO_2 foaming of pressure-induced-flow processed linear polypropylene

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ABSTRACT

Linear polypropylene is very difficult to foam due to its low melt strength and high crystallinity. Pressure-induced flow (PIF) has been demonstrated to be able to improve the foamability of linear PP under a very high pressure. In this study, we report a systematic evaluation to optimize PP foaming process using supercritical CO_2. PP was firstly processed by means of PIF at optimized conditions. For CO_2 foaming of PP, the effect of foaming pressure and saturation time was investigated in detail. A threshold foaming pressure of 13.8 MPa was found to be needed to achieve low-density foams. Comparing to commercially available EPP and high melt strength PP foams, the PIF PP foams possess much higher compressive strength and thermal stability at lower densities.

1. Introduction

The supercritical CO_2 ($scCO_2$) foaming process [1,2] of polypropylene (PP) has attracted plenty of attention from global industrial and academic researchers. However, PP is very difficult to foam because of its low melt strength and high crystallinity. Many methods such as polymer blends [3–5], composites [6–9], and copolymerization [10] have been used to achieve good expandable PP and PP foams. However, these methods face limited applications owning to the significant cost increase in materials and poor mechanical strength of foamed products in comparison with PP and other widely used foam materials such as polystyrene (PS). Recently, pressure-induced flow (PIF), a novel route to enhance the polymer strength, was devised to obtain excellent PP foams by our group [11]. PIF was firstly proposed by Gonzalez-Leon [12] and has been demonstrated that it is an effective method to markedly improve mechanical strength of various semicrystalline polymers and polymer blends [13–17]. Our previous work has shown, for the first time, that PIF is beneficial to $ScCO_2$ foaming of PP and a low-density PP foam with high performance was obtained. However, the PIF was conducted under very strict conditions such as very high pressure (>400 MPa) and long pressure holding time (1 h) and very long $scCO_2$ saturation time (>2 h) to realize the observed effect. These strict requirements greatly limited the potential industrialization of this technology. Furthermore, the study of PIF PP foaming process was still very limited so far.

Therefore, the optimization of PIF and $scCO_2$ foaming process of PP is necessary to overcome the major impedance for industrial-scale production. In this paper, a systematic study on a commercial PP resin was conducted. We optimized the material parameters and processing conditions. As a result, low-density PP foams with excellent mechanical and thermal stability properties under industrially relevant processing conditions were successfully achieved.

2. Experimental

2.1. Materials

PP with a melt flow index of 3 g/10 min was provided by LCY Chemical Company. CO_2 with a purity of 99.99% was received and used as a foaming agent.

2.2. PIF processing

The samples of size 50 mm (length) × 12 mm (width) × 2 mm (height) were placed in a homemade apparatus, which has a cavity of

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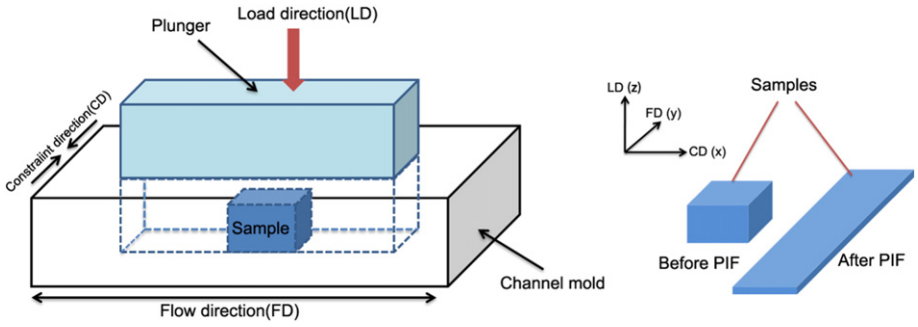

Fig. 1. [17] The schematic of the apparatus for PIF processing.

100 × 12 × 12 mm described in Fig. 1, and deformed at the temperature of 150 °C, pressure of 34.5 MPa and pressure holding time of 10 s. Other conditions were also tested for comparison. The obtained samples were used for further $scCO_2$ foaming and testing.

2.3. $ScCO_2$ foaming

The prepared samples from PIF processing mentioned above were batch foamed using a high-pressure autoclave. The specimens were placed in the high pressure vessel and then CO_2 was injected into the vessel. After the samples were saturated at certain temperature and pressure for a certain period of time, an instant depressurization was applied to achieve PP foaming. The effects of foaming pressure and saturation time on final foam density were studied.

2.4. Characterization

Foam density: The mass densities of foamed PP samples ρ_f were measured according to ASTM D792 involving weighing polymer foam in water using a sinker. ρ_f was calculated as follows:

$$\rho_f = \frac{a}{a-b}\rho_{water}$$

where a is the apparent mass of specimen in air, b the apparent mass of specimen completely immersed in water.

Scanning electron microscopy (SEM): The morphologies of the obtained PP foams were studied by SEM (Philips XL30). The samples were immersed in liquid nitrogen for 30 min and then fractured. The fractured surfaces were sprayed with a layer of gold for further observation by SEM.

Thermal mechanical analysis (TMA): The thermal stability of PIF and foamed samples were investigated by using a TMA (TA Instruments TMA 2940). The dimension change of samples was measured at a scanning rate of 5 °C/min from 30 °C to 180 °C under penetration mode.

Differential Scanning Calorimetry (DSC): A TA Q200 DSC was used to characterize the melting behavior of the PP foams with and without PIF processing. The scanning range was from 20 to 200 °C at a rate of 10 °C/min. Samples weighing 6–10 mg were used for DSC characterization.

X-ray Diffraction (XRD): The crystalline structure was investigated with an X-ray diffractometer (Bruker D8 Advance XRD) which has a Cu-ka radiation source and a wavelength of X-ray1.54 Å. The samples were scanned by 4°/min from 5° to 45° under 40 V and 50 mA.

Compressive test: Compressive strength of foams was conducted on an Instron 5569 Advanced Materials Testing system at room temperature according to standard ASTM D695.

3. Results and discussion

3.1. The effect of PP and PIF conditions on foam density

To make a comparison, several types of PP with different melt flow indexes (MFI) and slightly different crystallinity and melting temperatures were processed by PIF under the same conditions and thereafter the best PP was selected for further study at various PIF and foaming conditions to investigate the effect of PIF and $scCO_2$ on the foamability. The main material results are summarized in Table 1. It could be seen that PP with a low MFI showed better foamability. As the MFI increased, which meant lower melt strength, PP could still be foamed, but the foam density increased. A commercially available high melt strength PP, HMSPP (WB140 from Borealis) was also used for comparison. It could be foamed nicely without PIF, but the foam strength and thermal stability were poor (see Figs. 7 and 8). PP objects which were oriented to have a 'shish-kebabs' structure such as PP fibers and biaxially oriented PP (BOPP) films were also foamed to compare with PIF PP. The results in Table 1 showed that PP fibers and BOPP could not be foamed, which

Table 1
Comparison of foamability of different PPs with and without PIF.

PP	Melt flow index (g/10 min)	T_m (°C)	Crystallinity (%)	PIF conditions	Foam density(g/cm^3)
LCY PP1	3	169	37	150 °C, 34.5 MPa, 5 min	0.052
Dow PP	2	166	37.5	150 °C, 34.5 MPa, 5 min	0.091
LCY PP2	1.6	168	37	150 °C, 34.5 MPa, 5 min	0.062
LCY PP3	14.5		35	150 °C, 34.5 MPa, 5 min	0.18
LCY PP4	55	165	42	150 °C, 34.5 MPa, 5 min	0.21
WB140 (HMSPP)	2.1	163	35	Without PIF	0.025
PP fiber	N/A	147	17	Without PIF	0.92
Biaxial-oriented PP(BOPP)	N/A	164	32	Without PIF	0.93

Foaming conditions: 155 °C, 13.8 MPa, 2 h; N/A: not available.