Formation of Nanoscale Pores in Shish-kebab Structured Isotactic Polypropylene by Supercritical CO₂ Foaming

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Abstract:

In this article, a new technique combining polymer dynamic processing and low temperature foaming was proposed to fabricate isotactic polypropylene (iPP) foams with nano-scale cellular structures. A self-developed loop oscillating push-pull molding (LOPPM) device was first used to fabricate the highly oriented iPP samples with shish-kebab crystalline structure. A temperature-quench batch foaming device was used to foam the shish-kebab structured iPP sample at 100 °C with supercritical carbon dioxide (sc-CO₂) as blowing agent. Nano pores with average size of 55.3 nm were generated during foaming, attributing to the hindrance and nucleation synergistic effects of the shish-kebab crystalline structure. The LOPPM-PP foam samples showed high ultimate tensile strength (100% higher than PP) and strain-at-break (186% higher than LOPPM-PP), and excellent impact strength (658% higher than PP).

Keywords: Porous Materials; Microstructure; Mechanical Properties; Isotactic Polypropylene; Nanoscale Pores

1. Introduction

It is well known that with many polymers in their solid form, they are neither fully crystalline nor amorphous. The molecular chains of some crystalline polymer could be directed to form a special shish-kebab morphology under external shear force field [1]. The shish-kebab crystal possesses highly oriented polymer molecular chains as shish which are surrounded by plate-like lamellar crystals with periodic distance as kebabs [2, 3]. Polymers, such as polyethylene, polypropylene and polylactic acid, with shish-kebab crystalline structure showed elevated mechanical properties because of their highly compacted and oriented crystalline morphology [4-7].

Polymeric porous materials with nano-scale pores have attracted much attention because of their theoretical high-performance[8]. Microcellular foaming is a environmental friendly technique that capable to prepare submicro-scale polymeric foams based on organoclay-polymer nanocomposites or diblock copolymer as substrate materials [9-11]. However, there is still no literature report generation of nano pores in pure polymer substrate using microcellular foaming. The study of foaming behavior of shish-kebab structured crystalline polymer is rare. We believe the shish-kebab structured iPP substrate could interact with sc-CO₂ to create nanoscale pores by the hindrance effect of kebab lamellae when foaming at low temperature that keeps the crystal structure of iPP. Therefore, in this study, shish-kebab crystalline structured iPP substrates were prepared via a self-developed LOPPM device, then foamed at low temperature using sc-CO₂ to generate nanoscale pores within the iPP matrix for the first time. The morphology and mechanical properties of the samples prepared were characterized, and the mechanism of nano pore formation was elaborated as

well.

2. Materials and Methods

2.1 LOPPM Processing of iPP

The iPP (Injection grade, T30S) used in this study was purchased from Liaonin Huajing Ltd. with melt index of 3.20g/min at 230 °C (ASTM D1238). IPP samples with shish-kebab crystalline structure were prepared using a self-developed loop oscillating push-pull molding (LOPPM) machine that processes polymer melt under combined push-pull force field (high amplitude, low frequency) and oscillatory force field (low amplitude, high frequency), following the procedure in our previous study [12]. The molded samples were standard type I tensile test bars, and traditional PP samples were prepared using regular injection molding machine for comparison. At least five specimen were prepared under identical conditions for each test to ensure the repeatability.

2.2 Low Temperature Foaming Process

Samples prepared with LOPPM method were foamed using a home-made batch foaming device. They were placed in the cavity of the device and saturated with sc-CO₂ for 10 hours at 140 °C and 20 MPa, then the samples were cooled down to the foaming temperature of 100 °C and kept for 30 min. Finally, the samples were fast depressurized to ambient pressure followed by cycling cold water cooling. The mold cavity was large enough for samples to be foamed freely in all directions.

2.3 Characterizations

2.4.1 Scanning Electron Microscopy (SEM)

The LOPPM molded samples were freeze fractured in melt flow direction and surface

1 etched with H_2SO_4 , H_2NO_3 , KMnO_4 mixed solution for 2 hours. The foamed samples were
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3 directly freeze fractured in liquid nitrogen. All samples were sputter coated with a thin film of
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5 gold and observed with high resolution SEM (MERLIN, ZEISS).
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8 9 2.4.2 Wide angle X-ray diffraction (WXRd)

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11 WXRd (Rigaku Denki RAD-B) was used to test the crystal orientation of the iPP
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13 samples with or without shish-kebab structure. The wave length used was 0.154 nm and 2D
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15 images were obtained after scanning for 2 min.
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18 19 2.4.3 Mechanical Properties

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21 The tensile property of PP, LOPPM-PP and LOPPM-PP foam samples were
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23 performed on an universal mechanical testing machine (Instron 5566) with a crosshead speed
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25 of 10mm/min at room temperature according to ISO 527-2 standard. The notched izod impact
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27 test was carried out on a pendulum impact testing machine at room temperature following
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29 ISO 180 standard. The impact speed used was 3.35 m/s. Five samples of each group were
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31 tested at the same conditions. The average values were reported with standard deviation.
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40 3. Results and Discussion

41 42 3.1 Morphology of Solid Sample

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44 Figure 1 shows the microstructure of the solid samples after etching. Randomly
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46 oriented crystal lamellae were observed in traditional molded PP, as shown in Figure 1a. The
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48 WXRd results (Figure 1c) proved that traditional PP samples did not have any crystal plane
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50 orientation. However, it was easily to identify that a large amount of oriented crystal lamellae,
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52 i.e., shish-kebab crystalline structure, parallel aligned in the horizontal direction in the
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54 LOPPM molded sample (LOPPM-PP) (Figure 1b). This special kind of structure would be
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favorable for the enhancement of mechanical properties. The orientation of the crystal planes was proved by the symmetric arcs in the WXRD pattern (Figure 1d).

3.2 Nano Pore Structure after Foaming

Figure 2 shows the morphology of foamed LOPPM-PP sample (LOPPM-PP foam). As indicated in Figure 2a, the shish became more clear after foaming, and the cellular structures were found orientating along the shish with density as high as $3.83 \pm 0.54 \times 10^{15}$ pores/cm³, which is 5 to 10 orders higher than conventional microcellular foams. In high magnification image (Figure 2b), uniform nanoscale pores ranging from 20 nm to 100 nm were observed beside the shish clearly. The kebab lamellae were twisted or deformed by the expansion of gas and formed nano fibrous structure. The average cell diameter is 55.3 ± 18.2 nm which is the smallest pores ever prepared using sc-CO₂ foaming.

3.3 Mechanical Properties

The tensile and impact properties of traditional PP, LOPPM-PP and LOPPM-PP foam were tested and the results are shown in Figure 3 and Table 1. PP presents typical yield peak and the lowest ultimate tensile strength. The LOPPM-PP sample, however, had much higher modulus and lower strain-at-break without showing yield region because of its highly oriented rigid crystalline structure. For the LOPPM-PP foam samples, they showed the greatest elongation-at-break, higher ultimate tensile strength than PP and similar initial modulus to PP, indicating simultaneously toughening and reinforcement. The enhanced flexibility was attributed to the buffering effect of nanoscale pores. Moreover, the impact strength of LOPPM-PP foamed samples was the highest, followed by LOPPM-PP, while PP samples have the lowest impact strength as shown in Table 1. As indicated by the comparable

standard deviation to conventional injection molded PP sample, it is concluded that the samples made by LOPPM and LOPPM-foaming methods have good stability and reproducibility.

3.4 Mechanism of Nano Pore Formation

The mechanism of the nano pore formation is shown as Figure 4. In LOPPM processing, the molecular chains tend to orient and crystallize along the force field direction from their original coil structure, which would result in highly orientated shish-kebab crystalline structure. During sc-CO₂ saturation at low temperature, most crystals in the prepared iPP samples could be maintained at solid state, and the gas was mainly absorbed by the amorphous phase between lamellae kebabs which possess dense molecular array [13]. The lamellae acted as heterogeneous nucleation sites to induce more bubble nuclei and hindered the expansion of bubbles when depressurizing, which in together resulted in numerous nano pores.

4. Conclusions

In this study, iPP samples with shish-kebab crystalline structure were prepared using self-developed LOPPM device and subsequently foamed with supercritical CO₂ at low temperature to generate nanoscale cellular structure in the samples. Morphological results revealed that LOPPM processing could result in shish-kebab structured PP samples due to the combined external dynamic force field, and nano pores with size from 20 to 50nm could be obtained by foaming because of the hindrance and nucleation effects of the crystal lamellae. Mechanical tests results indicated that the samples with shish-kebab structure had higher modulus but lower flexibility, while the LOPPM-PP foamed samples showed moderate

modulus, high tensile strength and strain-at-break, and excellent impact strength.

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Figure Captions

Figure 1. SEM images (a-b) and WXRD patterns (c-d) of traditionally molded iPP (a, c) and LOPPM molded iPP (b, d).

Figure 2. Morphology of LOPPM-PP after supercritical CO₂ foaming. (a) low magnification image; (b) high magnification image.

Figure 3. Representative tensile curves of PP, LOPPM-PP and LOPPM-PP foam samples.

Figure 4. Schematic of shish-kebab structure formation in LOPPM processing and nanoscale pores formation during foaming.

Figure 1

Figure 2

Figure 3

Figure 4

Table 1. Tensile and impact tests statistical results of PP, LOPPM-PP and LOPPM-PP foam samples

sample	Tensile modulus (MPa)	Ultimate strength (MPa)	Strain-at-break (%)	Impact strength (MPa)
PP	219.7±31.3	18.8±6.4	131.17±12.3	3.2±0.4
LOPPM-PP	351.1±58.0	40.7±7.1	48.52±7.3	14.7±1.3
LOPPM-PP foam	207.6±50.8	37.0±7.3	137.22±11.9	23.9±1.6