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Formation of nanoscale pores in shish-kebab structured isotactic polypropylene by supercritical CO_2 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-CO_2) 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).

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-CO_2 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-CO_2 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 3.20 g/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

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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-CO_2 for 10 h 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

2.3.1. Scanning Electron Microscopy (SEM)

The LOPPM molded samples were freeze fractured in melt flow direction and surface etched with H_2SO_4, H_2NO_3, $KMnO_4$ mixed solution for 2 h. The foamed samples were directly freeze fractured in liquid nitrogen. All samples were sputter coated with a thin film of gold and observed with high resolution SEM (MERLIN, ZEISS).

2.3.2. Wide angle X-ray diffraction (WXRD)

WXRD (Rigaku Denki RAD-B) was used to test the crystal orientation of the iPP samples with or without shish-kebab structure. The wave length used was 0.154 nm and 2D images were obtained after scanning for 2 min.

2.3.3. Mechanical properties

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

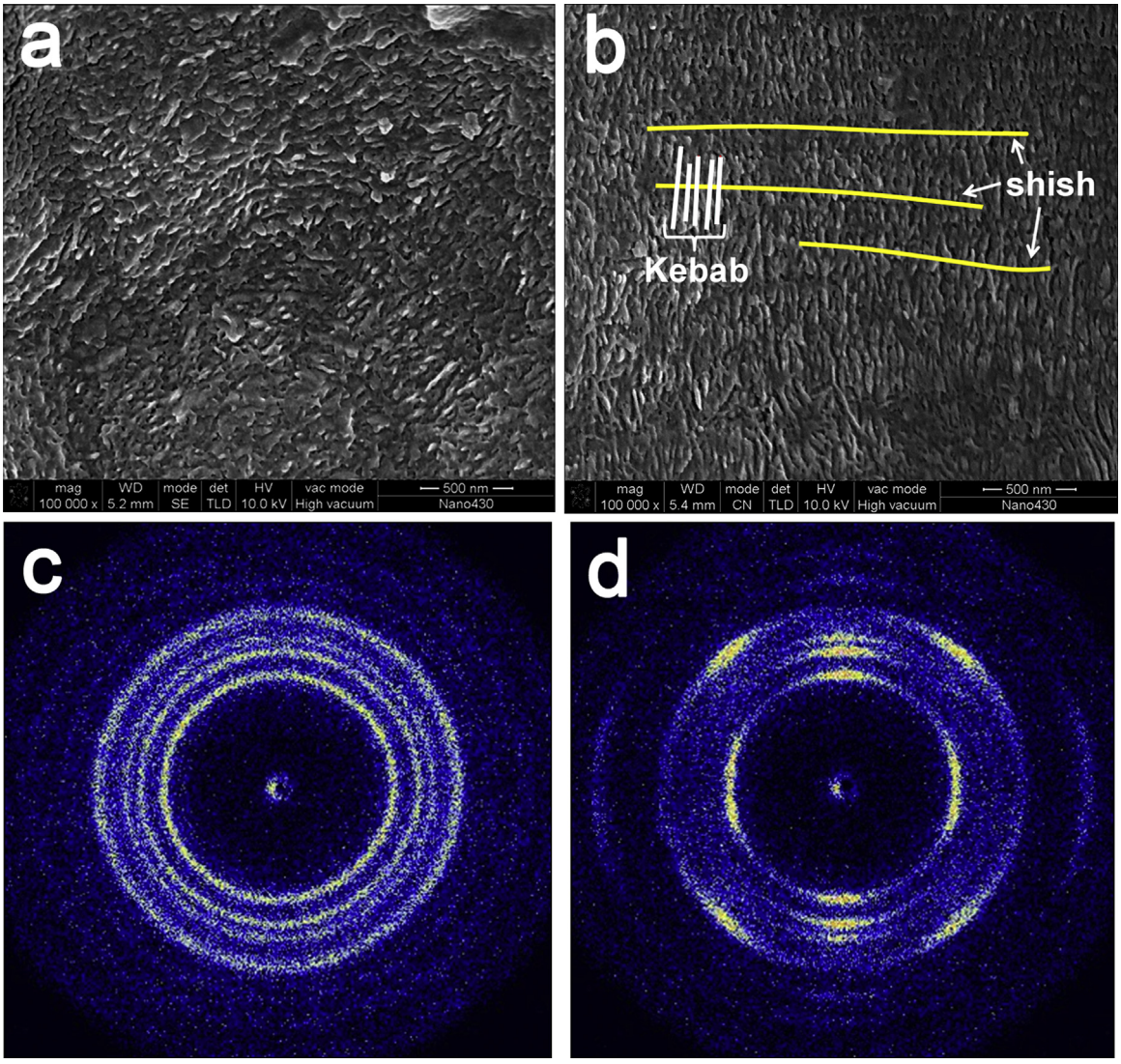

Fig. 1. SEM images (a–b) and WXRD patterns (c–d) of traditionally molded iPP (a, c) and LOPPM molded iPP (b, d).