Composites: Part B 51 (2013) 215–223

Contents lists available at SciVerse ScienceDirect

Composites: Part B

journal homepage: www.elsevier.com/locate/compositesb

In situ fibrillation of polymeric nucleating agents in polypropylene and subsequent transcrystallization propelled by high-pressure water penetration during water-assisted injection molding

Bin Wang, Han-Xiong Huang *, Zhi-Yong Wang

Lab for Micro Molding and Polymer Rheology, Center for Polymer Processing Equipment and Intellectualization, South China University of Technology, Guangzhou 510640, PR China

ARTICLE INFO

Article history:
Received 10 May 2012
Received in revised form 27 September 2012
Accepted 10 March 2013
Available online 22 March 2013

Keywords:
A. Polymer–matrix composites (PMCs)
B. Microstructure
B. Interface/interphase
E. Injection moulding

ABSTRACT

In situ microfibrillar reinforced composites (MFCs) parts of polypropylene (PP) and a special polymeric nucleating agent (acrylonitrile–styrene copolymer, SAN) with four weight ratios (PP/SAN; 98/2, 96/4, 94/6, and 92/8) were molded via water-assisted injection molding (WAIM). The phase morphology and crystalline structure of the WAIM MFCs parts were studied. It was found that high shear stress and cooling rate caused by the high-pressure water penetration during the WAIM could result in the in situ fibrillation of the SAN droplet, followed by the formation of transcrystals at the interface between the SAN microfiber and PP matrix. Moreover, β-form spherulites can be induced by the SAN. The contents of the transcrystals and β-form spherulites were dependent on the SAN content and melt temperature. Interestingly, a WAIM PP/SAN MFCs part with nearly half of its thickness totally dominated by transcrystals and the other half containing high contents of β-form spherulites can be obtained at proper SAN content and melt temperature. This work is expected to provide a promising way to tailor the crystalline structure of the molded parts.

1. Introduction

In situ microfibrillar reinforced composites (MFCs) based on two thermoplastics are successful examples of tailoring the microstructures of the parts for a desired application [1–3]. The MFCs are usually prepared by blending polyolefins with other polymers, especially engineering polymers like polyamide, poly(ethylene terephthalate) [4–7]. As for the mechanical properties, it is demonstrated that the MFCs show high modulus and strength [8–11], which can be ascribed to the presence of the high aspect ratio microfibers on one hand, and the good adhesion between the matrix and microfiber due to the formation of transcrystals on the other hand [12,13].

The preparation method of MFCs includes three basic steps [8,9,13]: (1) melt blending and extrusion of two immiscible polymers; (2) cold drawing of the extruded blend; and (3) the subsequent annealing of the drawn blend at constant strain and temperature range of $T_1 < T < T_2$, where T_1 and T_2 are the melting temperatures (T_m) of the two components. An external stretching force is a prerequisite for this method, and thus additional equipment is needed to provide the stretching force. Moreover, if the MFCs obtained by this method are used for injection and compression molding, the processing window is constrained between the T_ms of the microfibers and polymer matrix. This may be unfavorable for further processing the MFCs into desired parts. Consequently, a molding method that can produce MFCs parts by simply utilizing the internal shear and elongational stress caused by polymer melt flow is desired.

Recently, there has been increasing interest in a novel injection molding technique––water-assisted injection molding (WAIM) [14–16]. During the WAIM, the mold cavity is partially filled with the polymer melt followed by the injection of high-pressure water into the core of the melt. The high-pressure water propels the melt forward and displaces it within thick sections of the cavity. Just before de-molding, the water is released from the core to provide a hollow, but fully formed, geometry. The WAIM process is characterized by high shear stress and cooling rates due to the dynamic interactions of the high pressure water and polymer melt. It is found that the high shear and cooling rates caused by the high-pressure water penetration can induce the in situ fibrillation of the polyamide 6 (PA6) [17,18], the formation of the oriented crystalline structures [19,20], the orientation of glass fibers [21,22], and the formation of γ-form of the PA6/clay nanocomposites [23]. These fascinating findings lead to the idea that a MFCs part with high contents of transcrystals may be molded via WAIM. However, to the best knowledge of the authors, no relative studies have been reported yet.

In this work, polypropylene (PP) and acrylonitrile–styrene copolymer (SAN) were chosen as the polymer pairs for preparing MFCs parts via WAIM. Being confirmed to be an effective β-nucleating agent

* Corresponding author. Tel./fax: +86 20 2223 6799.
E-mail address: mmhuang@scut.edu.cn (H.-X. Huang).

1359-8368/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compositesb.2013.03.015

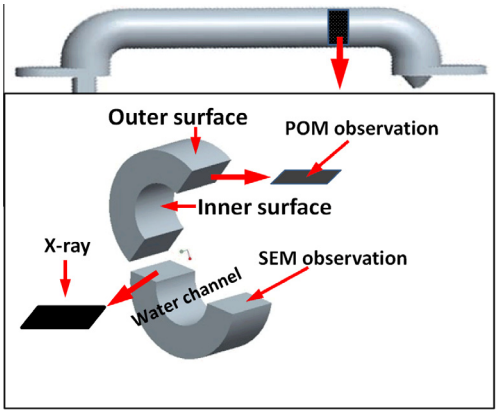

Fig. 1. Schematic of WAIM part and positions for SEM and POM observations.

[24,25], the SAN was expected to tailor the crystalline form of the PP matrix, besides the main roles of forming reinforcing microfiber and inducing the transcrystallization. So, the phase morphology and crystalline structure of the WAIM PP/SAN MFCs parts were studied, and the formation mechanism of the transcrystals was interpreted with the aid of stress and temperature fields within the mold cavity under high-pressure water penetration during the WAIM.

2. Experimental

2.1. Materials and sample preparation

The matrix polymer used in this work was an extrusion grade PP (grade F401, Petrochina Guangzhou Petrochemical Co.). Its melt flow index is about 2.3 g/10 min (at 230 °C and 2.16 kg). As the polymeric nucleating agents, an injection molding grade SAN (grade PN-117L200, Chi Mei Co.) with a melt flow index of 2.8 g/10 min (at 200 °C and 5 kg) was used.

The SAN was dried at 80 °C for 2 h in a vacuum oven. Then, the PP and SAN were dry mixed thoroughly before melt blending. The melt blending of PP and SAN at four weight ratios (98/2, 96/4, 94/6, and 92/8) was conducted using a single-screw extruder with a diameter of 20 mm. Two static mixers were connected to the extruder for the sake of further improving the mixing effect. The temperatures were maintained at 150, 200, 210, and 200 °C from the hopper to the die. After being pelletized and dried, the blends were molded using the WAIM equipment developed in our laboratory, which mainly consisted of a water injection unit and an 80-ton conventional injection molding machine with a highest injection rate of 84 cm^3/s [16].

The melt temperature was investigated in terms of its influence on the crystalline structure of the WAIM parts. Other processing parameters, including the short-shot size (64 vol%), water injection delay time (3 s), water injection pressure (10 MPa), and water packing time (6 s), were kept at constant. Both mold and water were kept at room temperature in all experiments.

2.2. Characterization

The WAIM PP/SAN MFCs parts were cut into segments of 5 mm length at a position near the end of the water channel (as shown in Fig. 1). The segments were used for the observations of both phase morphology and crystalline structure. For phase morphology observation, the segments were cryo-fractured along the flow direction in liquid nitrogen; the fractured segments were gold-

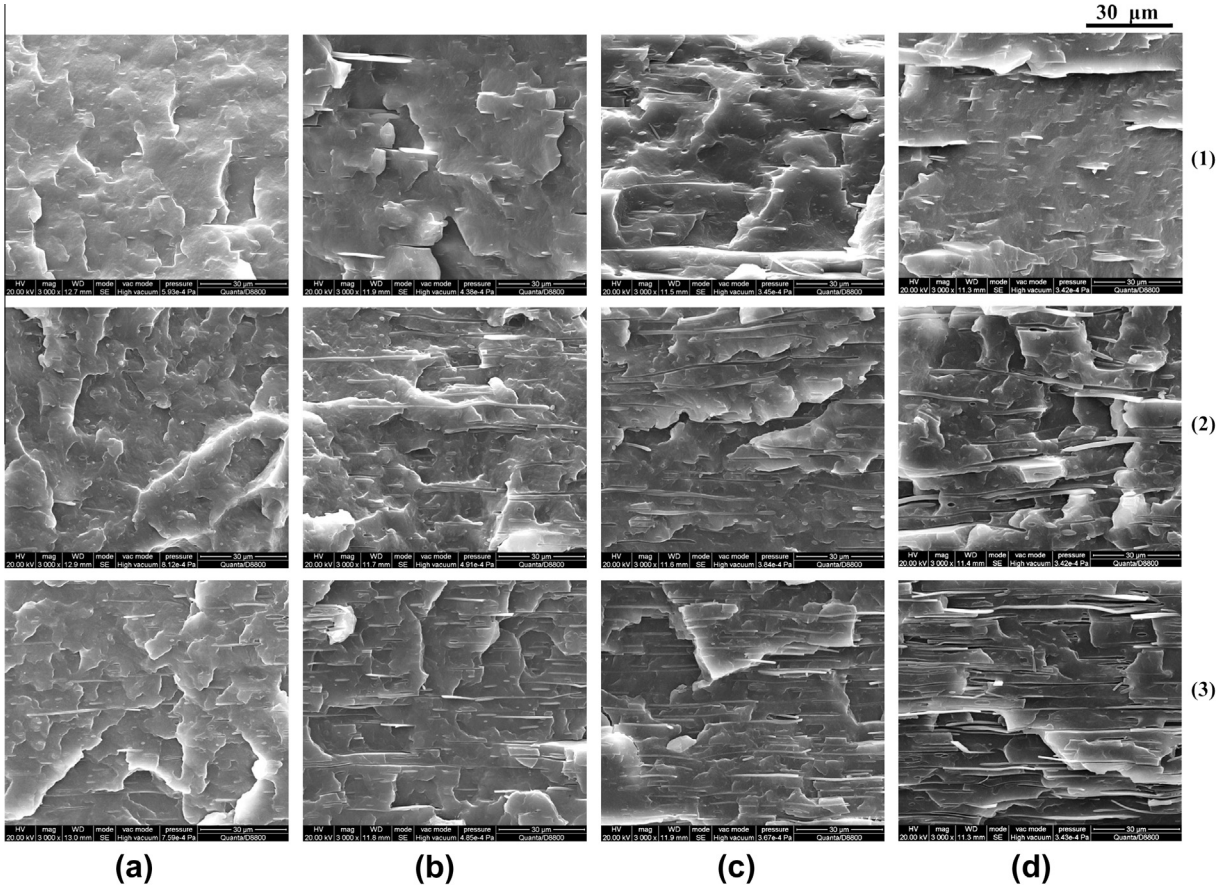

Fig. 2. SEM micrographs in (1) outer layer, (2) core layer, and (3) inner layer of WAIM parts of PP/SAN blends with four different weight ratios: (a) 98/2, (b) 96/4, (c) 94/6, and (d) 92/8. Melt temperature: 210 °C.