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Experiment and simulation of foaming injection molding of polypropylene/nano-calcium carbonate composites by supercritical carbon dioxide☆

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ABSTRACT

Microcellular injection molding of neat isotactic polypropylene (iPP) and isotactic polypropylene/nano-calcium carbonate composites (iPP/nano-$CaCO_3$) was performed using supercritical carbon dioxide as the physical blowing agent. The influences of filler content and operating conditions on microstructure morphology of iPP and iPP/nano-$CaCO_3$ microcellular samples were studied systematically. The results showed the bubble size of the microcellular samples could be effectively decreased while the cell density increased for iPP/nano-$CaCO_3$ composites, especially at high CO_2 concentration and back pressure, low mold temperature and injection speed, and high filler content. Then Moldex 3D was applied to simulate the microcellular injection molding process, with the application of the measured $ScCO_2$ solubility and diffusion data for iPP and iPP/nano-$CaCO_3$ composites respectively. For neat iPP, the simulated bubble size and density distribution in the center section of tensile bars showed a good agreement with the experimental values. However, for iPP/nano-$CaCO_3$ composites, the correction factor for nucleation activation energy F and the pre-exponential factor of nucleation rate f_0 were obtained by nonlinear regression on the experimental bubble size and density distribution. The parameters F and f_0 can be used to predict the microcellular injection molding process for iPP/nano-$CaCO_3$ composites by Moldex 3D.

1. Introduction

Microcellular foams, a kind of polymeric foam with bubble sizes less than 10 μm and bubble densities larger than 10^8 to 10^9 cm^{-3}, were introduced by Suh [1] in the 1980s to reduce material usage. However, maintaining the mechanical properties of microcellular polymeric foams as compared to solid materials still remains a major challenge today [2]. Polymer composite foams, on the other hand, have been regarded as a promising alternative to their neat resin foams due to their enhanced mechanical properties, better thermal stability, improved barrier properties, and superior flame retardancy [3–5]. Polypropylene/calcium carbonate (PP/$CaCO_3$) composites are widely used owing to the excellent properties of PP along with the low price of $CaCO_3$ [6,7]. The incorporation of $CaCO_3$ into PP not only increases the tensile strength of the composite, but also acts as an excellent crystal nucleation agent to enhance the impact strength of composites [8–11]. This makes PP/$CaCO_3$ composites a promising candidate for overcoming the mechanical weakness of foamed PP alone for industrial applications.

Microcellular injection molding technology has been successfully commercialized by Trexel, Inc. [12,13] to injection mold microcellular foams which can further improve the mechanical and thermal properties, such as higher strength/weight ratios, enhanced toughness, and increased impact strength [14–18]. Recently, an intensive research has been conducted on foaming processes employing environmentally benign blowing agents such as supercritical carbon dioxide (CO_2) and nitrogen (N_2). That is due to their unique properties such as being non-flammable, non-toxic, quick dissolving, and having high self-nucleating characteristics [19,20]. Furthermore, blending supercritical fluid (SCF) in a polymer melt can effectively reduce the viscosity, the glass transition temperature and the interfacial tension [21,22]. Thus, the foaming process can be operated at low temperatures and the degree of polymer degradation can be reduced [23,24]. Since the properties of molded polymer composites are affected by the processing conditions and the amount of filler, a finer cell structure and more uniform cell size distribution can be achieved by controlling the foaming processing conditions [25,26].

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For microcellular foaming process, there are numerous models of bubble nucleation and growth [27–36], among which the classic nucleation model and diffusion-induced bubble growth have been employed by the majority researchers for foaming process. By combining the bubble nucleation and growth model, Taki and co-workers numerically studied cell morphology the batch foamed PP by CO_2 [35,37]. Different from batch foaming process with static polymer melt, the bubble nucleation and growth in microcellular injection molding undergo macroscopic melt polymer flow. Thus, an appropriate fluid model should be combined with the classic nucleation model and diffusion-induced bubble growth during the injection molding process. The Mucell simulation function in the a CAE software Moldex 3D is a recent development of three-dimensional prediction of final bubble morphology with finite volume method in microcellular injection molding process, in which the capability of 3D Mucell prediction has been well validated with the experimental results of microcellular injection molding of polypropylene with supercritical nitrogen [10,11,38,39].

In this work, microcellular injection molding of isotactic polypropylene/nano-$CaCO_3$ composites was performed to investigate the microstructures of microcellular foams. The effects of the processing conditions, including the nano-$CaCO_3$ weight content, mold temperature, super-critical gas content, and injection speed, on the microstructures of microcells were studied. Then the Moldex 3D software was applied to simulate the microcellular injection molding process of neat polypropylene and polypropylene/nano-calcium carbonate composites respectively.

2. Experimental

2.1. Materials

Isotatic polypropylene (Pro-fax7523) with an average melt flow index (MFI) of 4.0 g per 10 min (230 °C, 21.6 N) was supplied by Basell Co., America. The filler, nano-$CaCO_3$ without surface treatment was purchased from Shanghai LingFeng Chemical Co., China. The primary particle size of nano-$CaCO_3$ is about 100 to 200 μm. TYZON TPT used as titanate compatibilizer, was provided by Dorf Ketal Chemical LLC, America. The physical blowing agent CO_2 (99.97%) was supplied by Airgas. Co., USA. All other materials were used as received.

The iPP was melt compounded with different weight contents of nano-$CaCO_3$ in a twin screw extruder (Leistritz, GmbH) at a screw speed of 50 $r \cdot min^{-1}$. The nano-$CaCO_3$ was organically pretreated with the titanate compatibilizer using the following process. First, 2 ml TYZON TPT was dissolved into 500 ml toluene with stirring at 45 °C for 4 h. Thereafter, 200 g of nano-$CaCO_3$ was added into this solution with stirring for another 6 h. The mixture was filtrated with Buchner funnel and washed several times using toluene. The rest of solvent was removed in a fume cupboard. Before compounding, the PP resin and the pretreated nano-$CaCO_3$ powder were dried in a vacuum oven at 80 °C for 12 h. For comparison, the neat PP for injection molding was also treated under the same process condition as the composites in the extruder.

2.2. Injection molding processing

The injection molding experiments were conducted on the injection molding machine (Arburg Allrounder 320) equipped with a MuCell SCF dosing system (Trexel, Inc., Wilmington, MA). Supercritical carbon dioxide ($ScCO_2$) was used as the physical blowing agents. The molding experiments were set to produce the standard ASTM-D638 tensile bars. The extruder barrel temperatures, from the hopper to the die, were set of 20, 175, 200, 220, and 220 °C, and the screw speed was 15 $m \cdot s^{-1}$.

Based on the experiment scheme as specified in Table 1, the iPP/nano-$CaCO_3$ composites with different contents of filler (2.5% and 5.0%) were injection molded for microcellular foams to investigate the effects of processing conditions (*i.e.* injection speed, mold temperature, and SCF weight percentage) on cell morphologies. A high CO_2 concentration was achieved by adjusting the pressure difference between the SCF outlet and the barrel [40]. The weight reduction was maintained at 15% for all the foamed parts, with proper control of the shot size. Also, the additional molding trial was made for solid parts at the same processing conditions with no CO_2 injection.

Table 1
Experimental design of foaming injection molding

Trial no.	Injection speed/%	Mold temperature/°C	Gas content/%	Sample name
1	5	10	HB 7%	HB 7%1
2	5	60	HB 7%	HB 7%-2
3	60	10	HB 7%	HB 7%-3
4	60	60	HB 7%	HB 7%-4
5	5	10	HB 5%	HB 5%-1
6	5	60	HB 5%	HB 5%-2
7	60	10	HB 5%	HB 5%-3
8	60	60	HB 5%	HB 5%-4
9	5	10	LB 5%	LB 5%-1
10	5	60	LB 5%	LB 5%-2
11	60	10	LB 5%	LB 5%-3
12	60	60	LB 5%	LB 5%-4

Note: HB is for high back pressure 5×10^6 Pa and melt pressure 13×10^6 Pa, while LB for low back pressure 3×10^6 Pa and melt pressure 9×10^6 Pa.
Maximum screw circumferential speed is 35 $m \cdot min^{-1}$.

2.3. Testing techniques

The micro-cellular structure of the molded parts was examined using a JEOL Neoscope Scanning electron microscopy (SEM) (Nikon Corp.) with an accelerating voltage of 10 kV. The SEM specimens (Fig. 1) were taken from the middle of the molded tensile bars by fracturing after being immersed in liquid nitrogen for 10 min and then spurted with a Pd (palladium) coating for 45 s. The average cell sizes and cell densities were obtained from the SEM analysis by the Image-Pro Plus 6.0 (Media Cybernetics, Silver Spring, MD) [21]. The number average diameter of all of the cells in the micrograph, d, was estimated using the following equation,

$$d = \frac{\sum d_i \cdot n_i}{\sum n_i} \quad (1)$$

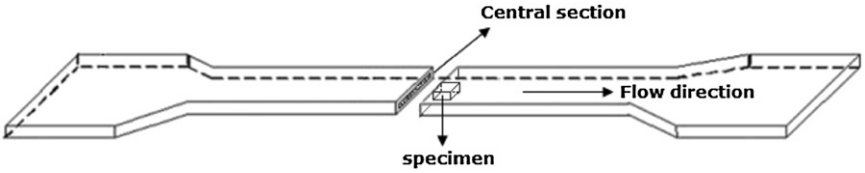

Fig. 1. Schematic of SEM specimen preparation.