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Full Length Article

Fabrication of high aspect ratio nanopillars and micro/nano combined structures with hydrophobic surface characteristics by injection molding

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ABSTRACT

Polymer products with micro/nano-structures have excellent mechanical and optical properties, chemical resistance, and other advantages. Injection molding is one of the most potential techniques to fabricate polymer products with micro/nano-structures artificially in large numbers. In this study, a surface approach to fabricate high aspect ratio nanopillars and micro/nano combined structures was presented. Mold insert with micropillar arrays and nanopillars on its surface was prepared by combing anodic aluminum oxide (AAO) template and etched plate. Anti-sticking modification was done on the template to realize a better demolding quality. The influences of mold temperature and polymer material on the final replication quality were investigated. The results showed that the final replication quality of high aspect ratio nanopillars was greatly improved as compared with the unprocessed template. Polymer with low elongation at break was not suitable to fabricate structures with high aspect ratio via injection molding. For polypropylene surface, the experimental results of static contact angles were almost consistent with Cassie-Baxter equation. When the mold temperature reached 178 °C, hair-like polycarbonate nanopillars were observed, resulting in an excellent hydrophobic characteristic.

1. Introduction

Products with micro/nano structures, such as microfludic chip, light emitting diode (LED) and self-cleaning surface, have a huge market potential in the fields of biomedicine, Micro-Electro-Mechanical System (MEMS), flexible electronics and etc [1–3]. The introduction of surface nanostructures would further improve the performance of these devices. Wettability is one of the most important characteristics that influence the flow behavior and the sensibility of their applications mentioned above. It is demonstrated that once the surface energy or the surface roughness is modified, dramatic changes in surface wettability would subsequently occur [4]. Super-hydrophobicity is a very important property for functional surfaces that has unique characteristics, such as water repellence, self-cleaning and reduction of drag. Inspired from the natural super-hydrophobic structures, such as lotus leaves, aquarius elongates legs and butterfly wings, more and more researchers have become interested in fabricating micro/nano-structures artificially [5–7].

Compared to the metallic material, polymer product has a lower surface free energy. Hydrophobic or even super-hydrophobic characteristics can be achieved as long as the hierarchical micro/nano-structures were fabricated on their surfaces. Because of the excellent workability, temperature resistance and high modulus of elasticity [8], it is very simple and diversified to fabricate micro/nano-structures on polymeric surface via injection molding, nanoimprinting, hot embossing and etc. Injection molding is one of the most potential techniques to fabricate polymer products in large numbers. When the feature size of the surface structure goes down to the nanometer scale, there exists significant differences in molding technologies. Due to the scale effect, the influences of the processing parameters on the replication quality are required for further investigation. Polymer melt in the mold cavity cools down rapidly because of the heat transfer from polymer to cold mold, thus prevents the filling of micro/nano-structures [9,10]. Meanwhile, a better control of the demolding quality is also essential by usually applying an anti-sticking coating layer on the mold insert, especially for the high aspect ratio structure [11–13].

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Conventional top-down techniques, including electron beam lithography, focused ion beam and LIGA (German acronym for Lithographie, Galvanoformung und Abformung) for fabricating mold insert with surface nanostructures are relatively expensive and complex. Simple and economical procedures are still required, such as the self-assembled method. Anodic aluminum oxide (AAO) template is a template with self-assembled hexagonal nanopores for good consistency. The depth, the diameter and other feature sizes of nanopores can be adjusted by varying the key processing parameters. Since Masuda [14] first proposed two-step anodic oxidization method for AAO template, the method has been increasingly used to prepare metallic or polymeric nanopillars and nanowires [15–17]. In order to reveal the feasibility, preliminary explorations have been undertaken by applying AAO template as a master for electroforming process [18] or directly as a mold insert for injection molding [19]. Instead of using a single mold insert that required more difficult fabrication techniques, the concept of assembled mold insert with different micro-features along the thickness direction was introduced in fabricating combined structures [20,21]. Regarding the micro/nano combined structures, previous studies have mainly focused on the replication quality of the microstructures [22,23]. There are only few reports in the injection molding process that concentrate on the potential wettability characteristics by using AAO templates with high aspect ratio nanopores as mold inserts.

In this work, a simple approach to the fabricate high aspect ratio nanopillars and micro/nano combined structures was proposed. The mold insert with micropillar arrays and nanopillar was prepared by combing AAO template and the etched plate. In order to guarantee a better morphology and demolding quality of the replicated structures, anti-sticking pre-treatment was done by utilizing the fluoroalkylsilane solution to form a low surface energy film. During the injection molding process, the influences of mold temperature and polymer material on the final replication quality were investigated. Considering the potential industrial application in self-cleaning, the hydrophobic characteristics of replicated surface was discussed by comparing the theory and the experimental results.

2. Materials and methods

2.1. Mold insert with micro/nano combined structures

The AAO template (AAO-SP-71, Shanghai Shangmu Tech., China) with high aspect ratio was utilized as the substrate layer of the mold insert. The diameter of surface nanopores was 400 nm and the depth was 5 um, with a pitch of 450 nm, as shown in Fig. 1b and Fig. 1c . The depth/diameter ratio of nanostructure was approximately 12:1. To avoid the influence of thickness nonuniformity during the injection molding process, the AAO template was polished to 200 μm. The mold insert carrying nanostructures was a 25 mm × 25 mm rectangle.

Mold insert with micro/nano combined structures was prepared by the combination of AAO template and the etched plate that acted as the upper layer, with a total thickness of 300 μm, as shown in Fig 1a. The stainless plate containing through-holes structure arrays of 200 μm diametral and 80 μm high pillars, in a square grid of pitch of 400 μm was obtained by the etching method based on a mask with circle array features.

2.2. Modification of AAO template

Compared to metallic mold insert, AAO template has a relatively low mechanical strength. Polymer melt is difficult to flow into nanopores. Adhesion phenomena frequently happen especially when the aspect ratio of nanostructures increases. In consideration of the filling difficulties and demolding defects, anti-sticking treatment was prepared on the template surface to reduce the surface free energy. Herein, a fluoroalkylsilane solution was prepared by mixing 0.5 g of 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (FAS-17, Nanjing Chengong Tech., China) and 49.5 g of ethanol for 3 h under continuous stirring at a low speed and room temperature. The prepared AAO template was washed and then immersed into the fluoroalkylsilane solution for 12 h before being dried in oven at 100 °C for 1 h.

Table 1
Main properties and processing parameters of PC and PP.

Main properties and processing parameters	PC Makrolon 2865	PP HD120 MO
Melt mass-flow rate(MFR, g/10 min)	9.5	12
Glass transition temperature (Tg, °C) or heat deflection temperature (HDT, °C)	148	88
Elongation at break (Eb, %)	50	80
Intrinsic contact angle (θ_Y, °)	82.3	100.0
Mold temperature (T_{mold}, °C)	163, 178	103, 118
Melt temperature (T_{melt}, °C)	295	240

2.3. Injection mold and materials for fabricating micro/nano-structures

The injection mold with a size of 126 mm × 126 mm was designed. Mold insert can be quickly installed by utilizing a pressing plate and a cover plate between the die inserts of moving and fixed halves. The method of electrical heating and oil cooling was applied to realize the variothermal technology. More details of the vario-thermal system and the installation of the mold insert can be seen from the previous studies [24,25]. Polymeric products with micro/nano combined structures were injection molded in a injection molding machine (Sodick® LD05EH2, with a max injection pressure of 197 MPa and a plunger diameter of 12 mm). The process overview in fabricating high aspect ratio nanopillars and micro/nano- structures is presented in Fig. 2.

For polymer materials with low elongation at break (Eb), such as PMMA Acrypet TF-8 (Eb = 3%) and COC Topas 5013S-04 (Eb = 1.7%), due to the relatively low tensile strength of high aspect ratio nanopillars, tensile failure phenomenon of the molded parts frequently happened. In order to avoid such fracture when the products were released from the mold cavity, two kinds of materials with excellent toughness property were selected. The main properties and processing parameters for each material were shown in Table. 1. For nano-injection molding process, the mold temperature is suggested to be about 20 °C higher than the glass transition temperature for amorphous polymer or the heat deflection temperature for crystalline polymer. For both materials, the injection velocity was 18 cm^3/s, the packing pressure was 80 MPa and the packing time was 5 s. In order to ensure a higher mechanical strength when the structure was released from the mold insert, the value of cooling time was set to 90 s.

2.4. Morphology and wettability characterization

The morphologies of mold insert and replicated polymer products were observed by using a field emission scanning electron microscopy (FESEM, Tescan Mira 3, Czech Republic). This microscopy is coupled with energy dispersive X-ray spectroscopy (EDS). Thus, the chemical composition can be also analyzed by Tescan Mira 3. The water contact angles were measured by using a contact angle meter (Attension Theta, Biolin Scientific, Sweden) in at least five different positions on the replicated samples after the surface cleaning procedure by ultrasonic cleaning method.