Rapid Replication of Nanostructures Made with Polymer Using Simple Injection Molding

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Abstract

It is possible to fabricate nanostructures with replication of 25.5 nm using injection molding. In this study, a silicon calibration grating was used as a mold insert to replicate high quality nanostructures using a simple custom-made injection machine. The replicated grating with 25.5 nm nanofeatures made with polymer was of high quality when a high mold temperature was employed and the mold was evacuated.

Keywords: injection molding, nanotechnology

1. Introduction

In recent years, a number of technologies for polymeric microstructure replication have been proposed, including the LIGA (lithography) process, which uses either hot embossing or injection molding to replicate polymeric microstructures. Some researchers have developed hot embossing and imprint processes for replicating nanofeatures ranging in size from 60 nm to 200 nm using polymers. Among the different molding techniques, injection molding is currently the most promising one due to its low cost and high precision in mass production. However, as most mold inserts have been fabricated using a LIGA process, the mold cost has been high. In addition, the high cost of the molding machines used to replicate parts has been a burden for most researchers. This research, thus, used an inexpensive calibration grating with 25.5 nm nanofeatures to investigate the moldability of polymers using a simple, custom-made injection machine. The grating costs only about US $100. It provides a simple way to replicate high quality nano-scale molded parts. Thus, it can save researchers considerable time and money.

The atomic force microscope (AFM) was used to calibrate the precision of the grating, made by the NT-MDT Co., Russia. Here, a square, silicon grating in a 3x3 mm² array, with a depth of 25.5 nm, a width of 1.5µm, and a pitch of 3µm, was used as a mold insert, as shown in Fig. 1. The mold insert made with silicon could continuously replicate parts because its strong mechanical properties resisted wear abrasion during molding. The
molded part, with nanofeatures made of polymethylmethacrylate (PMMA), was fabricated using a custom-made injection machine. PMMA polymer with a wide molecular weight distribution is produced, with an average molecular weight of around 90,000. Meanwhile, the melt transition temperature (Tm) of PMMA is 181.2°C. The custom-made hydraulic type injection machine included injection, melting, and clamping units. A vacuum pump was used to remove air or waste gas during forming. The experimental parameters included a forming pressure of 20 MPa and a processing temperature of 240°C. The mold temperature and evacuation of the mold were varied.

2. Results and Discussion

A molded part with nanofeatures made with PMMA included a sprue 6 mm in diameter, a runner 0.1 mm thick and 3 mm wide, and an active nano area of 3x3 mm², as shown in Fig. 2(a). The surface of the replicated nanostructures was characterized using AFM (Veeco CP-II, US). The AFM image in Fig. 2(b) shows that nanostructures with a depth of 25.5 nm, a width of 1.5 μm, and a pitch of 3 μm could be molded. The nanostructures with a depth of 25.5 nm were clearly formed to a measurement resolution of 1 nm. However, the molded nanostructures seem to have draft angles in the AFM profile. The shrinkage of the PMMA varied slightly between 0.4% and 0.7%, which induced draft angles in the nanostructures, but this was within the scope of the actual measuring accuracy. The draft angles of the molded nanofeatures could be reduced if the mold cavity was enlarged beforehand by 0.5% to compensate for the shrinkage effects on the polymer.

To understand the filling behavior of nano-scale molded structures, the depth-to-width ratio vs. the distance from the point of entry at different mold temperatures was shown in Fig. 3. If the molding process is optimized, the depth-to-width ratio of the molding structures (dimensionless) will be 0.017 for the grating cavity. The higher the depth-to-width ratio, the higher the quality of the nano-scale molded structures. This is desirable for generating uniform nanostructures throughout the surface of the grating. In every test, the depth-to-width ratio decreased slightly as the distance from the entry point increased. The molded nanostructures in the entry area had larger depth-to-width ratios for every flow trend because the local melt temperature and pressure close to the entry point of polymer melt were higher than those in other areas, which facilitated better filling of the polymer melt.

As can be seen, the depth-to-width ratios of the molded nanostructures were small at room temperature (25°C)
When the mold temperature was lower than the polymer glass transition temperature, a frozen layer formed as the molten polymer flowed into the cavity. In other words, a high mold temperature was needed to keep the cavity filled with molten polymer before the polymer froze. A mold temperature of 130°C, which was 30°C higher than the glass transition temperature of 100°C for PMMA, was adopted in the replication process. However, the depth-to-width ratios of the molded nanostructures were not as high as expected when a temperature of 130°C and no evacuation were employed in the mold. The depth-to-width ratio was only double that obtained at room temperature. In Fig. 4(a), the high-resolution AFM image shows that air bubbles were trapped in the molded polymer structures when the mold was not evacuated. Due to the trapped air, the depth-to-width ratio fell sharply when the flow was 1 mm from the entry point, as shown in Fig. 3. Subsequently, the mold was evacuated, and a higher mold temperature of 130°C was applied in the replication process. Through this, the depth-to-width ratio could be increased by 32%. In Fig. 4(b), the high-resolution AFM image shows that the replicated 25.5 nm nanofeatures were well formed and that trapped air was completely extracted.

In addition, the molding efficiency of mold temperatures of 110°C, 130°C, and 150°C, respectively, which were higher than the glass transition temperature of 100°C for PMMA was tested while the mold was evacuated. The average depth-to-width ratios in nanofeatures, as shown in Fig. 3, were 0.0146, 0.0152, and 0.0155 (compared to 0.017 in the original design), respectively, for mold temperatures of 110°C, 130°C, and 150°C. The molding efficiency was slightly increased by increasing the mold temperature. Nevertheless, the surface roughness of nanofeatures, as shown in Fig. 5, which was magnified in points A-A of Fig. 2(b), was Ra 2.6, 1.2, and 0.8 nm, respectively, for mold temperatures of 110°C, 130°C, and 150°C. As can be seen, the surface appearance of nanofeatures was shown to be rough in Fig. 5(a) when a temperature of 110°C was applied in the mold, while it was significantly improved when a higher temperature of 150°C was applied in the mold, as shown in Fig. 5(c). A higher mold temperature was shown to be able to effectively improve the surface roughness of nanofeatures. Past research [8-9] has come to the same conclusions, in that the injection molded samples were found to have a good surface appearance when a higher mold temperature was applied. In short, high quality nanostructures could be obtained using this economical custom-made injection machine under the optimum processing conditions.
which included a high mold temperature and evacuation of the mold. The obtained results reveal that a simple and inexpensive grating could be used as a mold insert to replicate nanostructures made with PMMA polymer.

3. Conclusions

A simple and cheap calibration grating with 25.5 nm nanofeatures could be used as a mold insert to replicate nanostructures using an economical, custom-made injection machine. Replicated nano-scale molded parts with clear structural definition were obtained under a high mold temperature and evacuation of the mold. The surface roughness of nanofeatures could be effectively improved by increasing the mold temperature to a level higher than the glass transition temperature of the polymer. The results show that the reproducibility of the nanostructures produced using injection molding was outstanding. This approach to the rapid replication of high quality nano-scale molded parts provides another choice for researchers and is a beginning step in this field of research.

References


Figure Captions

Fig. 1. SEM image of a silicon calibration grating with
nanofeatures having a depth of 25.5 nm, a width of 1.5 µm, and a pitch of 3 µm.

Fig. 2. (a) A molded part with nanofeatures made with PMMA, including a sprue 6 mm in diameter, a runner 0.1 mm thick and 3 mm wide, and an active nano area of 3x3 mm². (b) AFM surface profile of nanofeatures that are 25.5 nm deep (the depth has been exaggerated in the illustration).

Fig. 3. Experimental results for molding quality versus distance from point of entry under various mold temperatures.

Fig. 4. AFM images of a molded part which conducted in a mold temperature of 130°C (the depth has been exaggerated in the illustration). (a) Air was trapped in the nanostructures when the mold was not evacuated. (b) Nanostructures were well formed under evacuation of the mold.

Fig. 5. AFM surface profile of nanofeatures for magnifying points A-A in Fig. 2(b) conducted in different mold temperatures of (a) 110°C, (b) 130°C, and (c) 150°C.
Distance from entry point (mm)

Depth-to-width ratio (h/w×10⁻²)

- Mold temp. of 150°C and evacuation of the mold
- Mold temp. of 130°C and evacuation of the mold
- Mold temp. of 110°C and evacuation of the mold
- Mold temp. of 130°C and no evacuation of the mold
- Mold temp. of 25°C and no evacuation of the mold

Fig. 3

Trapped air

Fig. 4

Fig. 5
快速複製聚合物奈米特徵元件

利用射出技術成型奈米特徵元件 25.5 nm 之研究。在這研究中，利用材質為矽的校正規塊(calibration grating)做為模具模仁並利用自製射出機成型，具有奈米特徵結構校正規塊其成本只需 4000 台幣，即可製造出奈米特徵元件，省下許多昂貴的模具費用，複製高精度的奈米特徵結構。當複製出高精度 25.5 nm 聚合物特徵元件時，成型的深度隨著模具溫度影響，高的模具溫度較能被成型與分離。

關鍵詞：射出成型，奈米技術