Rapid Replication of Nanostructures Made with a Polymer Using Simple Injection Molding

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ABSTRACT: It is possible to fabricate nanostructures of 25.5 nm by replication using injection molding. In this study, a silicon calibration grating was used as a mold insert to replicate high-quality nanostructures with a simple custom-made injection machine. The replicated grating with 25.5-nm nanofeatures made with a polymer was of high quality when a high mold temperature was employed and the mold was evacuated. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 497–500, 2008

Key words: injection molding; nanotechnology

INTRODUCTION

In recent years, a number of technologies for polymeric microstructure replication have been proposed, including the lithographie galvanoformung abformung (LIGA) process (lithography), which uses either hot embossing[1] or injection molding[2–4] to replicate polymeric microstructures. Some researchers[5–7] have developed hot-embossing and imprint processes for replicating nanofeatures ranging in size from 60 to 200 nm through the use of polymers. Among the different molding techniques, injection molding is currently the most promising one because of its low cost and high precision in mass production. However, as most mold inserts have been fabricated with 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, therefore, used an inexpensive calibration grating with 25.5-nm nanofeatures to investigate the moldability of polymers with a simple, custom-made injection machine. The grating costs only about \$100. It provides a simple way to replicate high-quality nanoscale molded parts. Thus, it can save researchers considerable time and money.

EXPERIMENTAL

An atomic force microscope was used to calibrate the precision of the grating, which was made by NT-MDT Co. (Moscow, Russia). Here, a square silicon grating in a 3×3 mm^2 array, with a depth of 25.5 nm, a width of 1.5 μm, and a pitch of 3 μm, was used as a mold insert, as shown in Figure 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 poly(methyl methacrylate) (PMMA), was fabricated with a custom-made injection machine. A PMMA polymer with a wide molecular weight distribution was produced, with an average molecular weight of approximately 90,000. Meanwhile, the melt-transition temperature of PMMA was 181.2°C. The custom-made hydraulic-type injection machine included injection, melting, and clamping units.[4] 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.

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 nanoarea of 3×3 mm^2, as shown in Figure 2(a). The surface of the replicated nanostructures was characterized with an atomic force microscope (Veeco CP-II, New York). The atomic force microscopy (AFM) image in

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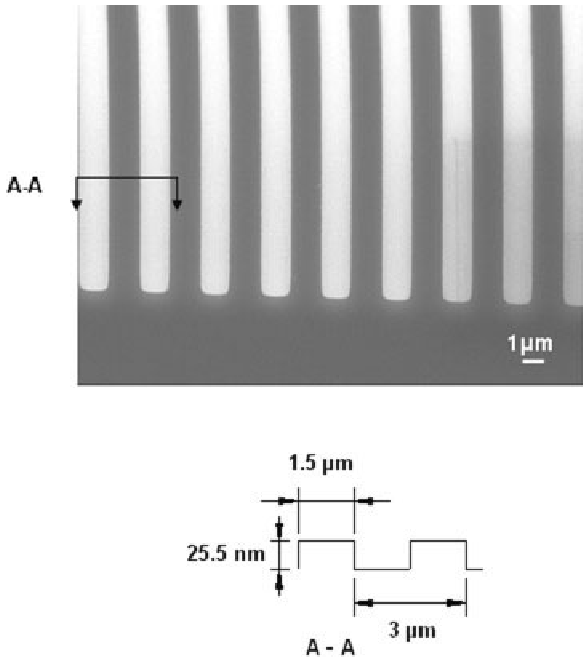

Figure 1 Scanning electron microscopy image of a silicon calibration grating with nanofeatures having a depth of 25.5 nm, a width of 1.5 μm, and a pitch of 3 μm.

Figure 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 seemed 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 were enlarged beforehand by 0.5% to compensate for the shrinkage effects on the polymer.

To understand the filling behavior of nanoscale molded structures, the depth-to-width ratio versus the distance from the point of entry at different mold temperatures is shown in Figure 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 is, the higher the quality will be of the nanoscale 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

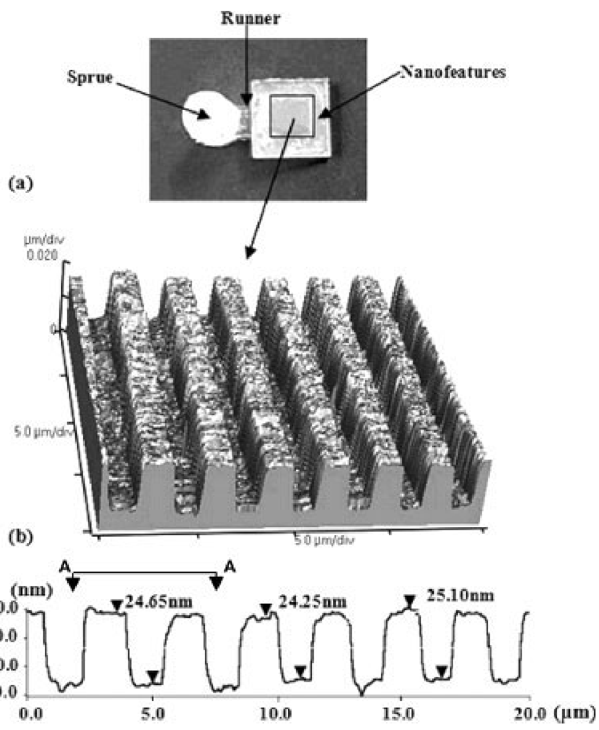

Figure 2 (a) Molded part with nanofeatures made with PMMA, including a sprue 6 mm in diameter, a runner 0.1 mm thick and 3 mm wide, and an active nanoarea of 3 × 3 mm^2, and (b) AFM surface profile of nanofeatures 25.5 nm deep (the depth is exaggerated in the illustration).

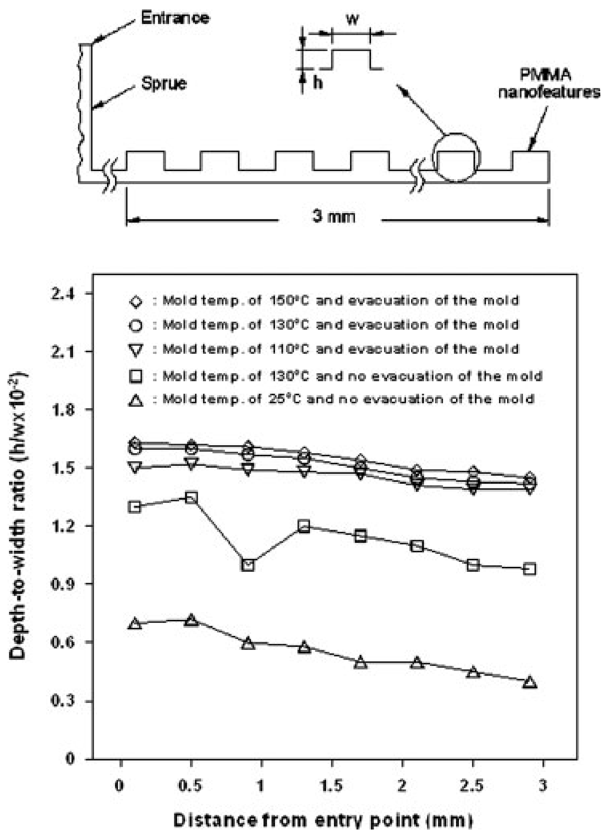

Figure 3 Experimental results for molding quality versus distance from point of entry at various mold temperatures.

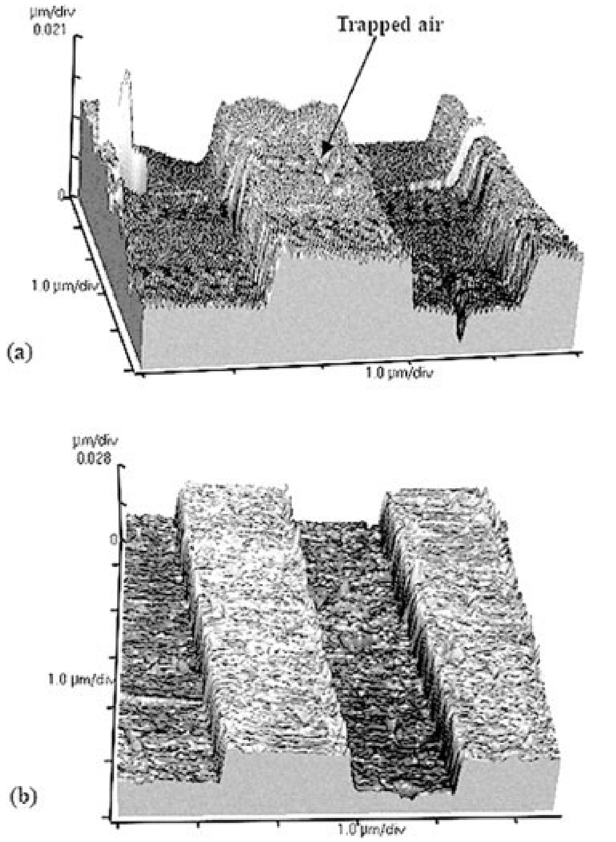

Figure 4 AFM images of a molded part made at a mold temperature of 130°C (the depth is exaggerated in the illustration): (a) air was trapped in the nanostructures when the mold was not evacuated and (b) nanostructures were well formed under evacuation of the mold.

were higher than those in other areas, and this facilitated better filling of the polymer melt.

The depth-to-width ratios of the molded nanostructures were small at room temperature (25°C) and with no evacuation of the mold. 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 Figure 4(a), the high-resolution AFM image shows that air bubbles were trapped in the molded polymer structures when the mold was not evacuated. Because of the trapped air, the depth-to-width ratio fell sharply when the flow was 1 mm from the entry point, as shown in Figure 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 Figure 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 at mold temperatures of 110, 130, and 150°C, 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 the nanofeatures, as shown in Figure 3, were 0.0146, 0.0152, and 0.0155 (vs 0.017 in the original design) for mold temperatures of 110, 130, and 150°C, respectively. The molding efficiency was slightly increased by an increase in the mold temperature. Nevertheless, the surface roughness of the nanofeatures, as shown in Figure 5, which was magnified in points A–A of Figure 2(b), was 2.6, 1.2, and 0.8 nm for mold temperatures of 110, 130, and 150°C, respectively. The surface appearance of the nanofeatures was rough, as shown in Figure 5(a), when a temperature of 110°C was applied in the mold, whereas it was significantly improved when a higher temperature of 150°C was applied in the mold, as shown in Figure 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,

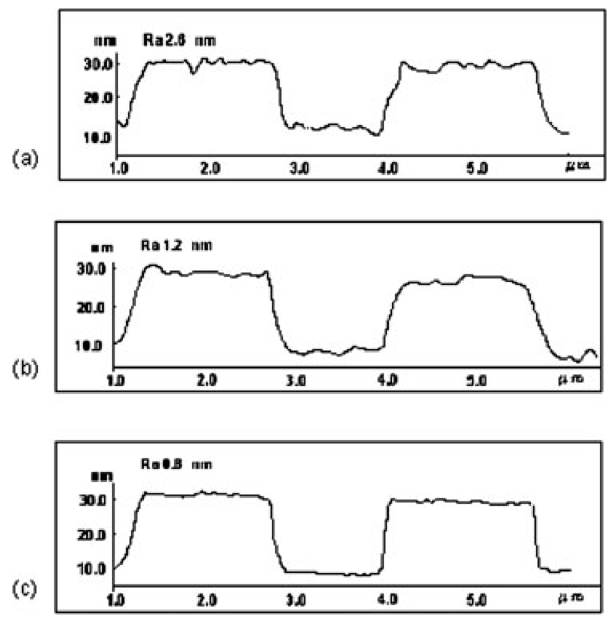

Figure 5 AFM surface profile of nanofeatures for magnifying points A–A in Figure 2(b) at mold temperatures of (a) 110, (b) 130, and (c) 150°C (Ra = surface roughness).

high-quality nanostructures can be obtained with this economical custom-made injection machine under the optimum processing conditions, which include a high mold temperature and evacuation of the mold. The obtained results reveal that a simple and inexpensive grating can be used as a mold insert to replicate nanostructures made with a PMMA polymer.

CONCLUSIONS

A simple and cheap calibration grating with 25.5-nm nanofeatures was used as a mold insert to replicate nanostructures with an economical, custom-made injection machine. Replicated nanoscale molded parts with clear structural definition were obtained under a high mold temperature and with evacuation of the mold. The surface roughness of the nanofeatures was effectively improved by an increase in 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 with injection molding was outstanding. This approach to the rapid replication of high-quality nanoscale molded parts provides another choice for researchers and is a beginning step in this field of research.

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