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Robust fabrication and evaluation of nanopattern insert molded parts

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ABSTRACT

Nanopatterning techniques have been developed for optical, magnetic, chemical, biological, and micro/nanoelectronic applications, where the verification of the nanopattern geometry is also critical for quality control of nanoengineered products. Nanopattern insert molding is a new method to produce nanopatterns on polymeric surface with high resolution, good productivity, and low cost. In this study, a disposable polymeric film, made of polyvinyl alcohol (PVA), was used as a stamp for replicating nanopatterns. In addition, a specialized image processing platform was proposed to characterize nanopattern structures, especially circular nanopillars with high accuracy and convenience. Such a tool was used for optimization of nanopattern processing conditions. The "shape dispersity index" was introduced to evaluate the replication quality in more systematic and robust manners.

1. Introduction

Fabrication of optical, magnetic, chemical, biological, and microelectronic devices requires high resolution transfer of micro and nanometer scale patterns on the surface [1–3]. The most common techniques for micro and nanostructure fabrications are imprinting, embossing, and injection molding. However, the imprinting and embossing take long processing time and have limitations in precision patterning onto the surface of polymers [4,5]. Injection molding is one of the most frequently employed processing methods for plastic parts [6,7]. On the other hand, micro and nanopatterns on the injection molded parts may be deformed and damaged by friction of a shrunk part at ejection, especially when the molded part has fairly large surface area. In the case where a steel mold with nanopatterns on its wall is used for replication, such limitation arising from the large surface area should be overcome, for instance by modifying the mold design for injection molding of nanopatterns [8].

As an alternative method to this problem, nanopattern insert molding (NPIM) utilizing advantages of both film insert molding (FIM) and nanoimprint lithography (NIL) was suggested in the previous study [9]. A PVA film with nanopatterns on its surface (PVA template) is inserted in the mold cavity, which is similar to FIM. The water solubility of PVA is utilized to remove the PVA template from the substrate. That is, after ejection, the PVA film can be dissolved with water from the nanopattern insert molded part. The nanopattern insert injection molding using the PVA template film is named NPIM. NPIM has the advantage of both the high precision char-

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acteristics of the nanoimprinting and mass production capability of the injection molding. It is also capable of producing curved parts possessing nanopillars with a high aspect ratio.

For a successful NPIM, remelting region must not exist in the template in order to copy the exact nanopattern from the template film. Nanopattern on the surface of the PVA film should be preserved during filling and packing stages. The injected resin needs to have a high melt flow index even at low temperature, and optimum processing conditions should be applied for NPIM [9]. For example, Monkkonen et al. reported that transparent COC, PC, and SBS resins are suitable for fabricating photonic nanostructures [10]. Although the nanopatterned PVA film is very thin, it inevitably causes nonhomogenous cooling, thereby resulting in the warpage of molded parts [11–14]. It is important to assess the nanopattern quality for engineering the NPIM process precisely. There are mainly two kinds of criteria in evaluating the quality of particle-type materials, i.e., size dispersity and positional dispersity. These dispersities do not make any difference in evaluating nanopattern quality because nanostructures such as nanopillars have almost the same radius and even distribution. For this reason, we propose a new concept, "shape dispersity" to better quantify the characteristics of nanostructures in this study.

There are limited reports on the evaluation of the nanopattern quality with use of highly sophisticated measurement devices such as scanning electron microscopy (SEM) and atomic force microscopy (AFM) which are generally used for observation of nano-scale structures. For evaluation of SEM images, there are several approaches to detect nano-size structures and extract the corresponding volumetric information automatically by using image analysis techniques. The first one is serial sectioning method [15], which uses SEM and focused ion beam (FIB) together. FIB first slices a specimen into several different layers, and then SEM captures the layers one by one. Thereafter, the images are merged into a 3D reconstructed model. The reconstructed 3D data can reveal volumetric information of the original specimen. This method has also been applied to a very complex-shaped object such as a chromosome successfully [16]. However, it has a shortcoming that it cannot be adopted to a bulky object such as nanostructure. Another example of the SEM image based analysis is to generate a 3D geometry by using two to four pieces of SEM images taken from different view angles. The 3D model can be formed using stereoview after proper image processing steps [17]. However, this method could not distinguish a target object from background. Therefore, such a stereoview based approach is not suitable for obtaining the volumetric information of nanopatterns.

A novel tool was developed in this study for the characterization of nanopatterns by introducing the shape dispersity that defines the quality of nanostructures in a quantitative fashion. Several imaging processing techniques [18,19], e.g., discrete wavelet packet transformation [20] and watershed algorithm [21], were also adopted in the calculation to extract shape information of nanopattern from SEM images. The nanostructures were fabricated using the NPIM process. To the best of our knowledge, this is the first research that not only fabricates nanostructures but also quantifies the quality of the nanopattern by using a single index. Overall, it is expected that the new procedure proposed should provide a new solid methodology for characterization of nanopattern, particularly at the interface of nanomaterial science and image processing techniques.

2. Experimental details

PVA (Aldrich, MW 70,000), a water-soluble synthetic polymer, was selected as the base material for the nanopattern template film. It is water soluble and has a melting point of 230 °C and a glass transition temperature of 85 °C for the fully hydrolyzed grade [6]. Cyclic olefin copolymers (COCs) produced by Polyplastics® were used as the raw material for injection molding. Topas® COC grade 5013 and 8007 used in this study had glass transition temperatures of 80 and 130 °C, respectively, and their melt temperature for injection was in the range of 190–250 and 240–300 °C. The melt flow index (MFI) of COC 8007 and COC 5013 is 32 ml/10 min and 48 ml/10 min at 260 °C under 2.16 kgf [22,23]. However, COC 8007 has better fluidity at low temperature of around 200 °C.

Fig. 1 shows the NPIM procedures to fabricate nanopatterns on the surface of an injection molded part. Silicon masters which contain nanoscale holes were fabricated by the e-beam lithography and the polycarbonate replica of the Si master was prepared by UV lithography. The positive polycarbonate replica fabricated by the UV-NIL had the surface topology opposite to the Si master with concave cylindrical nanoscale holes. The polycarbonate replica had convex nanopillars at the surface, and a 5% PVA aqueous solution was poured over the polycarbonate replica that had been placed in a stainless steel tray by applying the Molecular Transfer Lithography (MxL). It was dried in vacuum and heated on a hot plate for 6 h at 60 °C to obtain a PVA template film. The negative PVA template films with thickness of about 100 and 200 μm were peeled off from the first polycarbonate replica and cut into rectangular slabs of 50 mm × 50 mm [24,25]. The nanopatterned PVA template film was installed into one side of the mold cavity as in the case of FIM, and the polymeric resin was injected into the cavity. The sacrificial PVA template film was dissolved by hot water for about 30 min at 60 °C after ejection of the part. Prior to injection molding, COC 8007 and 5013 resins were pre-dried and dehumidified for 6 to 12 h at 60 and 80 °C.

NPIM was conducted by employing an injection molding machine (SE75D: Sumitomo Heavy Industries Ltd.), and the molding conditions are listed in Table 1. The melting temperatures of resin and mold were determined for successful nanoinjection molding. The polymer melt temperature was selected as 240, 260, and 280 °C from recommendation of the resin producer (Polyplastics®). The mold temperature was maintained at 50, 70, and 90 °C by considering the glass transition temperature of PVA. Strirojpinyo et al. [23] demonstrated that mold temperature had little effect, and Pranov and Rasmussen [26] reported that

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