A Micro-nano Melt Transcription Molding Process to produce Thermoplastic Devices with Tens Nanometers Scale Fine Patterns

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A Micro-nano Melt Transcription Molding Process (MTM) was developed to produce highly functional thermoplastic devices with fine patterns on their surfaces. By taking advantage of fluidity, wettability and low modulus of molten thermoplastics, the patterns with the dimensions from tens nanometers to hundreds micrometers or millimeters with high aspect ratio (Aspect = height/diameter or width) and sharp edge could be molded under high productivity. The nano hole arrays, which have the walls with width (W) 60 nm × height (H) 270 nm (Aspect 5) and W45 nm × H320 nm (Aspect 7) that partition the holes with diameter 250 nm, could successfully be molded by using both PMMA (Polymethylmethacrylate) and PC (Polycarbonate). The well patterns for cell culture with W15 μm × 120 μm (Aspect 8) were molded uniformly over the surface area 100 mm × 125 mm with the cycle time in one minute and a little. As a result, it was confirmed that MTM proposed in this study could be applied effectively to the practical production of thermoplastic devices which have the surface patterns in a high grade and under high productivity.

Keywords: thermoplastic device, nanometer, fine pattern, transcription, molding

1. Introduction

Plastic devices with fine patterns on their surfaces with the dimensions from nanometers to micrometers scale have the potential application in the promising and growing field such as medical product, bioscience, optics, semiconductor, flat-panel display, data storage media or solar energy parts, etc. Fabrications of fine patterns are utilized to the control of optical properties such as reflection, refraction, diffraction or deflection, to the control of surface functions such as hydrophobic or hydrophilic properties, and to the miniaturization for high density data storage, MEMS, LSI or μ-TAS. Making use of these advantages potentially bring about significant improvement of performance and/or creation of new function to the products, and as a result, commercialization of highly profitable plastic devices. As the fabrication methods of fine patterns on the plastic products, several molding processes have been used such as hot embossing, UV-imprint, injection molding and/or roll-to-roll process, etc. However, the practical production of wide range of high quality fine patterns from tens nanometers to hundreds micrometers or millimeters under high productivity by using large extent of thermoplastics adapting to the final usage was not achieved sufficiently.

In this study, we propose a new molding process MTM to adapt to the practical production of high quality fine patterns. And we verified experimentally its performance by using stamps with fine patterns of high aspect ratio from tens nanometers to hundreds micrometers.

2. Micro-nano melt transcription molding

Fig.1 illustrates the molding cycle of MTM[1]. It consists of plasticization of thermoplastic pellets by screw, coating it uniformly over the heated stamp on which fine patterns are fabricated, compression and cooling of coated polymer for transcription, and releasing the molded products from the stamp.
By taking advantage of fluidity, wettability and low modulus of molten polymer, the fine patterns with high transcription ratio, high aspect ratio, sharp edge, uniform transcription over the surface, dimensional stability and low residual stress could be obtained under high productivity. Large extent of thermoplastic pellets such as amorphous and/or crystalline polymers, high fluidity and/or high viscosity(high strength or high molecular weight) grades, polymer alloys and compounding can be used. Furthermore the accurate thickness control of molded products from 100 μm to 5mm, and transcription of wide range of pattern dimensions from tens nanometers to hundreds micrometers or millimeters could be achieved. The molten thermoplastics just after plasticized by the plasticization unit are supplied everywhere of the surface fine patterns of the stamp through the die with the same temperature of molten plastics, and without any temperature drop during coating. Then the uniform transcription over the large surface area could be possible.

3. Experimental

3.1 Materials

Materials used were PMMA[Parapet EH1000, Tg= 110 ℃, MFR =1.3g/10min (230 ℃,37.3N), Kuraray Co. Ltd.] and PC[Panlite AD-5503, Tg=142 ℃, MVR = 54cm³/10min (300 ℃, 12N), Teijin Chemicals Ltd.].

3.2 Stamps

Silicone stamp with nano pillar arrays was prepared with minimum space between pillars 45nm, their height 320nm(Asp7.1) and diameter of pillars 250nm as shown in Fig.3. The stamp size is 4 inch diameters and patterned area is 5mm squares. Nickel stamp with nano pillars was prepared with minimum space between pillars 60nm, their height 270nm(Asp4.5) and diameter of pillars 250nm. The stamp size is 70mm squares and patterned area is 5mm squares.
Nickel stamp with Anti Reflective (AR) patterns with aperture and pitch 250nm and Depth 325nm (Asp 1) was prepared. Stamp size 120mm squares and patterned area 100mm squares.

The Ni stamp which has well patterns for cell culture with \( W_{15\mu m} \times \text{Depth}_{120\mu m} (\text{Asp 8}) \) over 100mm \( \times \) 125mm was prepared by Kuraray Co.Ltd.. Furthermore, the stamps which have micro slits with \( W_{10\mu m} \times \text{Depth}_{30\mu m} (\text{Asp 3}) \) and micro pillars with Diameter \( 10\mu m \times \text{Depth} \ 30\mu m (\text{Asp 3}) \) were also prepared.

3.3 Equipments

The molding machine used to the experiments of MTM process was MTM II 130-30 (Maximum compression force: 130 kN, max. stamp size: 148.5mm \( \times \) 24mm) manufactured by the Japan Steel Works, Ltd. as shown in Fig. 4. It consists of plasticization and injection unit, compression unit, coating unit, base mold and its heating and cooling unit, etc..

Fig. 4. Photograph of MTM II 130-30.

3.4 Molding conditions

Important parameters on the molding conditions of MTM process are molten polymer temperature, stamp temperature for transcription and demolding, compression pressure and compression time. They were adjusted adequately with accordance to the material properties such as glass transmission temperature and/or visco-elasticity, and dimensions of the patterns fabricated on the stamp.

4. Results and Discussion

4.1 Nanometers scale fine patterns

Fig. 5 shows AFM images of nano hole arrays molded by using PMMA and the silicon stamp as shown in Fig. 3 under the condition with polymer temperature 270°C, stamp temperature 145°C, compression pressure 1MPa and compression time 10s. The walls that partition the holes were successfully molded. The wall width was 45nm, and its heights were 317nm at triangular and 318nm at square arrangement respectively. Transcription ratio (height of molded patterns / depth of the patterns of the stamp) was over 99%.

The same results were obtained in case of PC by changing the stamp temperature.

Fig. 6 shows SEM images of nano pillar arrays fabricated on Nickel stamp(a) and that of nano hole arrays molded by using PC under the condition with polymer temperature 270°C, stamp temperature 165°C, compression pressure 2MPa and compression time 10s. The width of the walls that partition the holes was 60nm and their height was 270nm[3]. Transcription ratio was 100%.

Transcription performance of MTM process was evaluated with regard to the dependence of transcription ratio on the stamp temperature, pressure and its applying time during coating and compression stages. Furthermore storage modulus \( G' \) and loss modulus \( G'' \) of the PC polymer were measured by using rotational rheometer.
Fig. 6. Scanning electron microscope images of nano pillar arrays on Nickel stamp (a) and molded nano hole arrays by using PC. Holes with 250nm diameters are partitioned by the walls with 60nm width and 270nm height (b).

(Anton Paar GmbH) at angular frequency $\omega = 37.3\text{rad/s}$ which was determined by the shear rate $\dot{\gamma}$ (s$^{-1}$) calculated to fill the spaces that partition the nano pillars of the stamp as shown in Fig.6 (a). The transcription moldings only by the coating stage (without compression) and those by both the coating and compression stages were tried.

Fig. 7 shows the experimental results. When using both coating and compression stages, the perfect transcription was achieved at lower stamp temperature 160°C by increasing compression pressure from 2MPa to 8MPa or compression time from 10s to 20s at which $G'$ and/or $G''$ was smaller than 10MPa. On the other hand, perfect transcription only by the coating stage was achieved under very low coating pressure 0.04MPa and its very short applying time 0.36s at the stamp temperature higher than 175°C. $G'$ and $G''$ at this temperature were almost smaller than 1MPa. Low $G'$ and $G''$ itself, however, is guessed to be one of the necessary conditions for the perfect transcription but not the sufficient conditions, and it does not necessarily assure perfect filling of polymer into the recess of stamp.

We think that fluidity and wettability are the specific features of molten thermoplastics in contrast to solid films. They are guessed to be the "driving force" of MTM process that enabled rapid filling of molten polymer into the recess of the stamp with width tens nanometers to hundreds nanometers, and with high aspect ratio under very low pressure and in short time.

Fig. 8 shows SEM images of AR patterns fabricated on the Nickel stamp (a) and that of molded AR patterns by using PC [4]. AR patterns of aperture and pitch 250nm and height 325nm were perfectly molded under the condition with polymer temperature 270°C, the stamp temperature 165°C, compression pressure 0.5MPa and compression time 1s. The compression pressure and time was much lower and shorter respectively compared to the condition of nano hole arrays in shown in Fig.5 due to smaller aspect ratio and larger dimensions of AR patterns.

Fig. 8. Scanning electron microscope images of AR patterns on Nickel stamp (a) and molded patterns made of PC with aperture and pitch 250nm and height 325nm by using MTM (b).
Perfect transcription of AR pattern shown in Fig.8 just only by the coating stage was achieved at the stamp temperature 165°C under the same coating pressure and its applying time with the case of nano hole arrays in Fig.7. The difference of 10°C, also, will probably be due to smaller aspect ratio and larger dimensions.

As a result, it was confirmed that tens and/or hundreds nanometers scale fine patterns with high aspect ratio could almost perfectly be molded under very low compression pressure and in short compression time both in the case of PMMA and PC by using MTM process.

4.2 Micrometers scale fine patterns

Fig.9 shows the well patterns for cell culture produced by Kuraray Co. Ltd.[5]. Width and height of the walls that partition the wells are 15µm and 120µm(Asp8) respectively. The material used was polystyrene(PS), the thickness of product was 300µm. They were successfully molded uniformly over the surface area 100mm×125mm in 1 minute and a little.

Fig.9. Micro-space plate used for three-dimensional culture system of human hepatocytes produced by Kuraray Co. Ltd.[5]. The plate has 200µm×200µm×50µm square compartments on its culture surface. The width and height of the walls that partition the wells are 15µm and 120µm(Asp8) respectively.

Fig.10 shows 12 pieces of chips with micro slits molded by using PMMA. The width of the micro slit is 10µm and its height is 30µm(Asp3). Thickness of the product is 250µm. All the chips were perfectly molded at the condition with molten polymer temperature 270°C, stamp temperature 165°C, compression pressure 11 MPa and compression time 11s. Necessity of higher pressure compared to nanometers scale fine patterns comes from the relatively larger deformation of micrometers scale patterns compared to nanometers scale. The higher the compression pressure, the shorter the compression time required to the sufficient transcription.

Fig.10. Photograph and SEM images of micro slits molded by using PMMA. The thickness of molded product is 250µm, the width and height of slits are 10µm and 30µm respectively(Asp3).

Fig.11 shows the dependence of transcription ratio of micro slits shown in Fig.10 made of polycarbonate on the stamp temperature. Although the compression pressure and time were the same as those of Fig.7, the perfect transcription was achieved at the stamp temperature 5°C higher. And both coating and compression were indispensable for perfect transcription of micro slits. This will be due to the necessity of larger deformation in case of micro slits compared to nanometers scale fine patterns.

Fig.11. Temperature dependence of transcription ratio of the micro slits with W10µm×H30µm(Asp3), and that of storage and loss modulus of PC.

Fig.12 shows 2 pieces of circular chip with micro pillars molded by using PMMA. The diameter of the chip is 36mm, the size of the pillar is φ10µm×height 30µm(Asp3) and the pitch between the pillars is 20µm. Thickness of the molded product is 200µm. All the pillars were molded perfectly with the sharp edges of the pillars at the condition with molten polymer
Fig. 12. Photograph and SEM images of micro pillars molded by using PMMA. The thickness of the molded product is 200 μm. Diameter, height and pitch are 10 μm, 30 μm and 20 μm respectively (Asp3).

temperature 280 °C, stamp temperature 160 °C, compression pressure 11 MPa and compression time 15s. Molding defects such as stretching, breakage, bending or flash were not observed.

As a result, it was confirmed that tens or hundreds micrometers scale patterns with high aspect ratio could also be perfectly molded by using MTM in short time with relatively higher pressure compared to nanometers scale patterns.

5. Conclusions

We proposed a new molding process MTM to mold thermoplastic devices which have high grade fine patterns on their surfaces under high productivity. The principal advantages of MTM come from making effectively use of fluidity, wettability, adhesive force and/or low modulus of molten plastics to mold high grade fine patterns.

Nano hole arrays partitioned by the walls with W 45nm × H 320nm (Asp7.1), the diameter of the hole 250nm, were successfully molded under the low compression pressure 1MPa, short compression time 10s and the stamp temperature 145°C in case of PMMA. The well patterns for cell culture partitioned by the wall with W 15μm × H 120μm (Asp8) made of PS could be molded uniformly over the surface area 100mm×125mm in the cycle time 1 minute and a little.

We conclude that the MTM could be utilized to the manufacture of thermoplastic devices having high quality fine patterns with high aspect ratios and sharp edges with the dimensions from tens nanometers to hundreds micrometers or millimeters uniformly over their surfaces by using various kinds of thermoplastics under high productivity and with low cost.

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References