

MICROMOLDING ON CURVED SURFACES WITH THERMOPLASTICS*

Bang-kun Jin, Xiao-song Wu, Ping-sheng He** and Li-jia Pan

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China

Abstract Microstructures were produced on curved surfaces and micro-protrusions by using direct micromolding with four thermoplastic polymers. This method is simpler and more convenient than micromolding with liquid prepolymer or using the μ TM method. By repeated molding, crossed structures were produced with a stamp prepared only with lines. The processing variables including the softening temperature of the polymers and heating time were discussed. The result shows that the optimal molding temperature is preferably slightly higher than the melting temperature of the thermoplastic polymers, at which polymers are in the critical states of being melted. This method can be applied to many polymers except those with high softening temperatures or high rate of shrinkage upon temperature change.

Keyword Soft lithography, Micromolding, Polydimethylsiloxane, Thermoplastics

INTRODUCTION

Microfabrication is now becoming more and more important due to the impending requirements of modern science and technology, especially in the field of opto-electronics and microelectronics^[1–3]. As a newly developed method, soft lithography has many advantages as compared with the traditional photolithography^[3–7]. For example, it is of low-cost and needs no costly equipment, the process is simple and easy to operate, and large-area patterns can be made in a single operation. Especially, soft lithography can circumvent the side-effect of diffraction of light and break the 100 nm line-width limit in photolithography. This is significant for the fast development of nanotechnology. Soft lithography can also transfer micro-patterns easily onto non-planar surfaces. Though there have been many reports about the research and applications of soft lithography, most of them tried to make micro-patterns with liquids or prepolymers^[2, 8, 9]. However, during the process of polymerization or the evaporation of solvent, the transition from Van der Waals distance (0.3–0.5 nm) to chemical bonding distance (a typical distance of C—C bond is 0.154 nm) will result in a large volume contraction, *e.g.*, even polymers like epoxy compounds have more than 20% volume contraction during polymerization^[10]. This kind of contraction will undoubtedly distort the surfaces of the micropatterns.

For polymer solutions with high concentrations, the evaporation of a large amount of solvent will also induce the shrinkage of the surface. So it would be more advantageous to pattern structures on the surface of polymers directly. Fortunately, due to the thermoplasticity of polymers and the superior heat resistance (–100°C to 250°C) of stamp materials — polydimethylsiloxane (PDMS) — compared to most of the thermoplastics^[11], micro-structures may be fabricated directly on the surfaces of a thermoplastic material by micromolding. Previously, we have briefly reported the micromolding of linear microstructure on surfaces of polyethylene^[12]. In this paper, we further fabricate microstructures on surfaces, including curved surfaces and micro-protrusions, of four different kinds of thermoplastics by micromolding. A regular micro-point array was also produced with a line-patterned stamp by double stamping in different directions. Effects of the variables including molding

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** Corresponding author: Ping-sheng He (何平笙), E-mail: hpsm@ustc.edu.cn

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temperature and heating time on the micromolding were also investigated. Besides, the curing behavior of PDMS stamp materials were monitored in order to optimize the ratio of PDMS to hardener and curing conditions of stamp materials.

EXPERIMENTAL

Materials and Experiments

The thermoplastics used were all available commercially. They are low-density polyethylene (LDPE) 1F7B (Yanshan Petrochemical Co., China); polypropylene (PP) FY4012 (Polyolefin Company, Singapore); polystyrene (PS) (Lanzhou Petrochemical Co., China); poly(methyl methacrylate) (PMMA) (Longxin Chemicals, China). The organic silicone rubber, polydimethylsiloxane SDM-801, used as the stamp materials and the hardener were obtained from Chenguang Institute of Chemical and Engineering, Sichuan, China. The glass master model plates with the microlines on the surface were prepared by normal photolithography by the National Synchrotron Radiation Center, the University of Science and Technology of China, Hefei.

A home-made HLX-1 resin curemeter was used to monitor the curing process of PDMS and to optimize the ratio of PDMS to hardener as well as the best curing conditions^[13–15]. Micromolding on thermoplastic polymers was conducted on a hot-plate controlled by a thermostat. Photographs were taken with an X-650 scanning electronic microscope and a Rathenow optical microscope, respectively.

It should be emphasized that, in this experiment, the temperatures were measured from the center of the hot-plate, which may be about 10°C higher than the apparent temperatures on the surface of the hot-plate.

RESULTS AND DISCUSSION

Optimization of the Ratio of PDMS/Hardener

The elastomeric stamp is the key element in the soft lithography technology, which directly affects the accuracy of the replicated microstructures. A good stamp should have both enough rigidity and a certain elasticity, so that it can maintain its shape during the stamping process while making conformal contact with the substrate. In this experiment, organic silicone rubber made of PDMS, which is usually used as mold glue, was used to make the elastomeric stamp. In order to obtain PDMS with good physical properties, a home-made resin curemeter^[13–15] was used to monitor the curing process of PDMS and to optimize the ratio of hardener to PDMS. Figure 1 shows the isothermal curing curve of PDMS with respect to different contents of hardener at 60°C. The horizontal coordinate is curing time, and the vertical coordinate is the torque required to turn the PDMS by a small angle, which corresponds to the modulus or the viscosity of the PDMS, and can be regarded as a relative criterion of the curing degree. So the curing curve reflects the extent of the curing process. The point where the curve first deviates from the horizontal baseline is regarded as the gel point, the corresponding elapsed time is the gel time t_g . As the curing process proceeds, the torque (modulus) increases gradually and reaches a plateau region after some time, where PDMS has cured completely and the corresponding time elapsed is termed the full curing time t_c . With increasing content of hardener from 2.0% to 3.5%, t_c decreased from 116 min to 34 min and the torque (modulus) simultaneously increased due to the growing number of crosslinking points. However, when the content is greater than 3.5%, the PDMS will cure too quickly to be operable, whereas when the content is less than 2.0%, PDMS will require much more time to be cured, and the torque (modulus) of the cured PDMS is too low. It is noted that after the completion of curing, PDMS containing 2.5% of hardener has nearly the same torque (modulus) as that containing 2.0% of hardener. At lower content there are not enough crosslinking points in PDMS to reinforce its strength. This indicates that only when the content of hardener reaches a certain value can the PDMS have enough rigidity. Comparing the changes of curing speeds and the torque (modulus), it is suggested that the optimal ratio of PDMS/hardener is 2.5%–3.0%. The stamp made with optimal content of hardener proves to have the desired rigidity and flexibility in our experiment.

Preparation of Elastomeric Stamp

PDMS and the hardener in a ratio of 100:3 (W/W) were mixed thoroughly. The mixture was vacuum evacuated

for about 10 min to remove the embedded air bubbles, and then was cast onto a glass master plate made by the photolithographic technique. After curing at room temperature for more than 8 h, the PDMS stamp was peeled off carefully and a replica of the microstructures were formed on the surface of the PDMS stamp. Figure 2 shows the SEM graph of the surface of the master and the PDMS stamp cast from it. It can be seen that they have a very similar appearance.

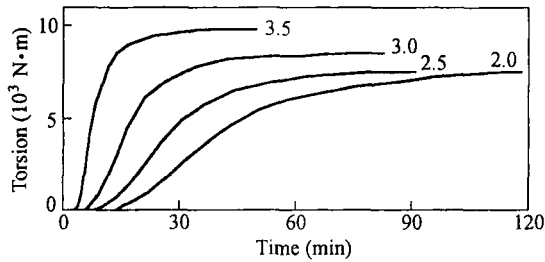


Fig. 1 Cure curve of PDMS with different content of hardener at 60°C

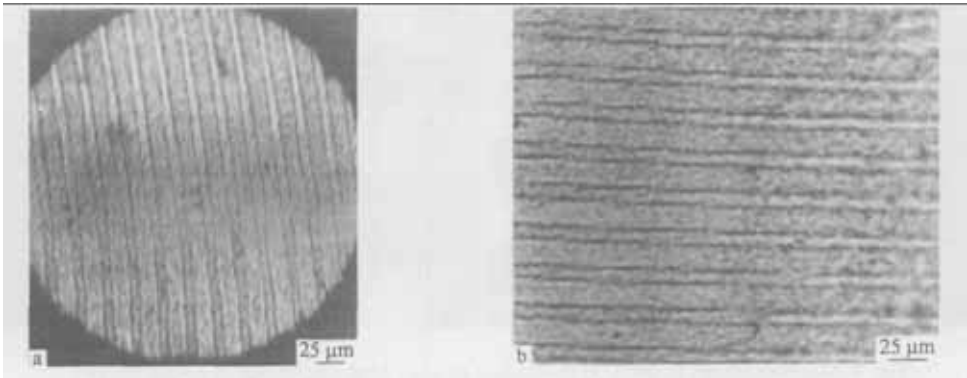


Fig. 2 SEM graph of the surface of master(a) and PDMS stamp (b)

Micromolding on Curved Surfaces

With soft lithography, various microstructures have been made with liquids or prepolymers^[8, 9]. Here we have succeeded in fabricating microlines on the curved surfaces with four kinds of thermoplastics directly by micromolding. To do so, a glass stick with a diameter of 5.0 mm was used to provide the curved surface. Thermoplastics pellets, the glass stick and the elastomeric stamp were placed separately on two microscopic glass slides and heated to a presetting temperature (a little higher than the softening temperature of the thermoplastics) on the hot-plate. As soon as the thermoplastics pellets softened, they were scraped onto the surface of the stick, and heating continued for a little while. Then the elastomeric stamp was pressed on the softened pellets with an appropriate force, and the pellets were taken away from the hot-plate to cool down to room temperature in the air. After peeling off the stamp carefully, the microstructures on the stamp were seen to have been transferred onto the surface of the thermoplastics. Figure 3 is the micro-patterns micromolded on the curved surface of the glass stick with LDPE (a) and PS (b). Distinct sharp lines with a little curvature can be seen clearly. The curvature of the lines can also be obviously seen from the change of line-width and the change of brightness. For polymers with low fluidity at their melting temperatures, such as PS, it is important to make the samples into an even film on the stick first. Otherwise, after preheating, they could not spread out evenly and made the stamping difficult.

Molding Micro-stripes on Micro-Protrusion Raised by a Capillary

Although it is thought to be a big challenge to transfer micropatterns onto the surfaces of smaller curvature^[16], micromolding is capable of doing this task very well. In this work, a glass fiber with a diameter of about 0.20 mm was placed on the glass substrate to form a micro-protrusion, and micromolding was carried out on it with four polymers, *i.e.* LDPE, PMMA, PS and PP according to the above procedures. Figure 4 shows the resulting

photographs, in which the central columns under which there are glass fibers embedded exhibit clear lines, which are nearly the same as those in the other parts of the pictures. However, due to the strong crystallization tendency, the surface of the PP microstructure is somewhat coarse. This result proves that micro-patterns could be produced on the curved surface with curvature on the sub-micron scale by micromolding.

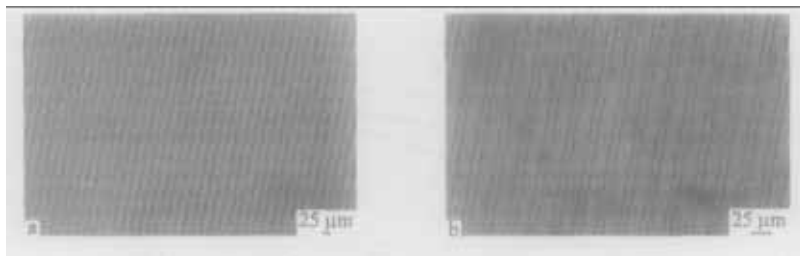


Fig. 3 Photos of microstructures micromolded on curved surfaces
a) LDPE at 150°C, b) PS at 180°C

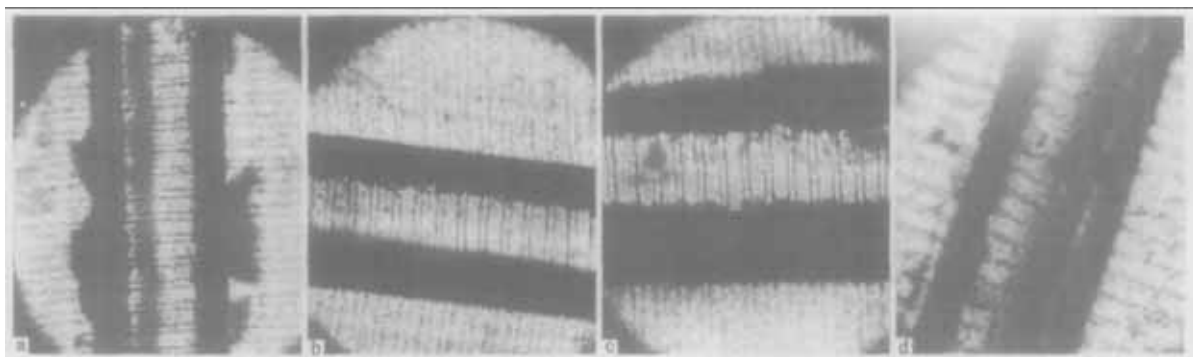


Fig. 4 Microstructures molded on the surface of glass fiber (the period is 25 μm for all)
a) LDPE (at 150°C); b) PMMA (at 190°C); c) PS (at 180°C); d) PP (at 190°C)

Being different from μTM ^[8] and MIMIC^[9], micromolding implies the fabrication of microstructures on the common polymer surface directly instead of using polymer precursors or polymer solutions, so this method is more convenient. The mechanism of this method is based on the thermoplasticity of polymers and the capillary force^[17] in the microchannels of the stamp. Upon softening, polymers will fill the microchannels automatically; after cooling down, the structures are solidified on the surface. In the micromolding process, preheating of the stamp is indispensable, otherwise there would be many bubbles or holes left on the molded surface of the polymer because the air adsorbed on the surface of PDMS stamp would expand and be expelled out while heating, which affects the quality of the microstructures significantly. Due to the good heat resistance, each elastomeric stamp can be used up to 50 times in thermal micromolding before it deteriorates.

However, it is difficult to obtain distinct patterns with crystallizable polymers and polymers with high shrinkage rate during temperature change. For example, microstructures as small as 3 μm cannot be made on the surface of crystalline polymer, acetal copolymer POA. It is the amorphous polymers, such as PS and PMMA that have good moldability giving clear microstructures or patterns by micromolding.

Production of Crossed Microstructures (Array of Dots) by Double Molding

More complex patterns can be produced on thermoplastics by repeated molding with a single stamp embossed with only line patterns. The stamp and PS pellets were heated to 150°C separately, then the stamp was pressed on the PS, both of them were removed from the hot-plate to cool down for about 20 s. After then, they were heated separately for a little while, and the second stamping was quickly applied to the PS film at the direction cross to the first molding. Thus an array of polymer dots can be obtained. If different stamps with different period are used in the two steps, multilevel dot-patterns with different line widths and heights are obtained. Figure 5(a) is

the resulting pattern of double cross molding with a single stamp, Fig. 5(b) is the resulting pattern of double cross molding with two different stamp I ($12.5\text{ }\mu\text{m}$ width $\times$ $2\text{ }\mu\text{m}$ depth) and stamp II ($25\text{ }\mu\text{m}$ width $\times$ $1\text{ }\mu\text{m}$ depth). Note that the square patterns in Fig. 5(a) turned round because of the shrinkage of PS above glass transition temperature. In this process, temperature and heating time must be paid much attention. Too high a temperature or too long a heating time may over-soften the first-time molding and make the first-layer pattern blur, while with too short a heating time the second stamping cannot be successfully applied.

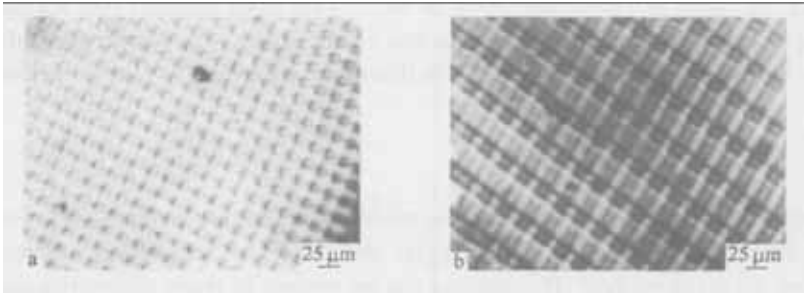


Fig. 5 Array of dots molded on PS with a stamp (a) and two different stamps (b)

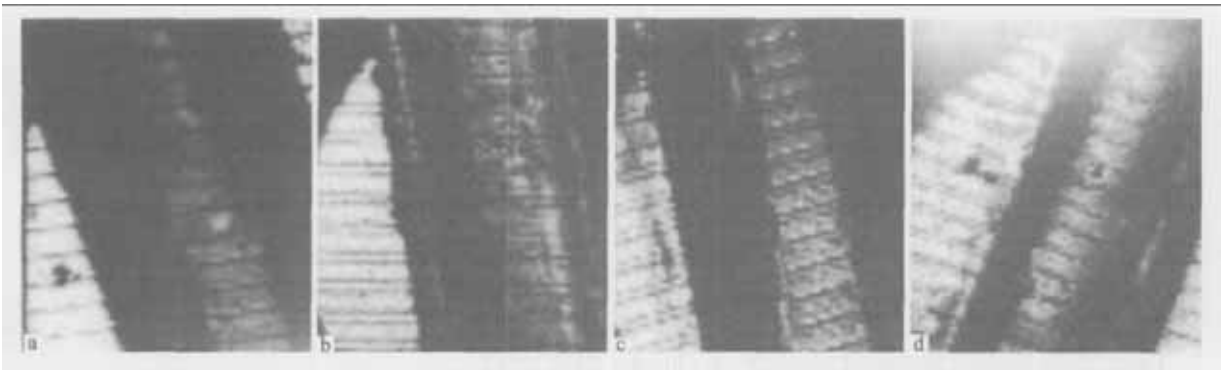


Fig. 6 Micromolding on PS at different temperatures (the period is $25\text{ }\mu\text{m}$ for all)
a) 170°C ; b) 180°C ; c) 190°C ; d) 200°C

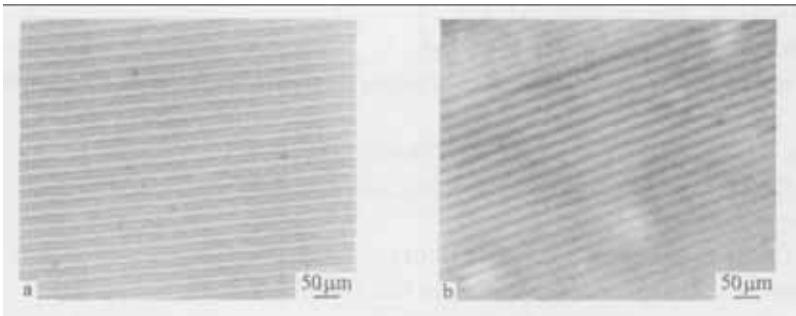


Fig. 7 Micromolding on LDPE with the stamp heated at a temperature different to that of LDPE, (a) stamp at 96°C and LDPE at 103°C , (b) stamp at 103°C and LDPE at 96°C

Effect of Molding Temperature

Temperature is an important factor in micromolding that strongly affects the quality, *i.e.* sharpness and clearness, of the microstructures produced on polymer surfaces. Too low a temperature cannot soften the pellets enough to replicate the pattern, while too high a temperature would make the thermoplastics melt thoroughly or even destroy the elastomeric stamp. When heated at 210°C , the PDMS stamp turns black quickly, the boundary between pattern area and non-pattern area blurs and the colorful diffraction pattern disappears. This means that the stamp is destroyed. Figure 6 shows the photographs of patterns molded with PS at different temperatures. In

the Fig, it can be seen that lines are indistinguishable at 170°C because the lines are very shallow; while at 200°C the lines begin to blur; the clearest pattern is obtained at 190°C. Nearly the same phenomena can be seen on LDPE. By varying the molding temperatures, it is found that the most suitable molding temperature is one that is slightly lower than the melting temperature of the polymer, at which the polymers are in the critical states of being melted. Also we have attempted the molding of polymers with the stamp and polymer heated at different temperatures, Fig. 7 shows the results for LDPE. The patterns molded with the stamp at 96°C and LDPE at 103°C are better than with the stamp at 103°C and LDPE at 96°C. This result suggests that during micromolding the temperature of the polymer is more important than that of the stamp. The temperature of polymers must be decided accurately in order to get clear patterns, while that of the stamp can be somewhat lower so as to prolong its service life.

CONCLUSION

We have demonstrated that microstructures can be made on the curved surfaces or micro-protrusions with thermoplastics by micromolding directly. It is simpler and more convenient than micromolding with liquid prepolymer or using the μ TM method. This method can be applied to many polymers except those with high softening temperatures or high rate of shrinkage upon temperature change.

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