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用微模塑直接在聚合物曲面上制备微图形*

潘力佳， 金邦坤， 何平笙**， 陈 磊
（中国科学技术大学高分子科学与工程系，合肥 230026）

摘 要： 用聚二甲基硅氧烷制备的，表面复制有微图形的'弹性印章'直接在聚乙烯，聚丙烯，聚苯乙烯和聚甲基丙烯酸甲酯等热塑性聚合物表面上进行热微模塑，无需复杂设备并可在普通实验室条件下，复制微图形，甚至在小试管外壁的曲面上或在用毛细管形成的微突起表面上也能制备出微曲面图形. 讨论了不同聚合物对生成微图形的影响，认为结晶性聚合物以及在温度变化时有较大收缩率的聚合物在微模塑中难以获得清晰图形. 无定形聚合物如聚苯乙烯和聚甲基丙烯酸甲酯等能够获得清晰的微结构.

关键词： 微模塑；聚乙烯；聚丙烯；聚苯乙烯；聚甲基丙烯酸甲酯

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Making the Micro-patterns Directly on a Curved Surface of Polymer by Micromolding*

Pan Lijia, Jin Bangkun, He Pingsheng**, Chen Lei
(*Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei* 230026)

Abstract Micro-patterns on curved surfaces were generated by molding on molten polymers with a cured polydimethylsiloxane elastomeric stamp. Microstructures were easily and repeatedly produced with four thermoplastics of polyethylene, polypropylene, polystyrene and poly(methyl methacrylate) on some curved surfaces, even on the surface with a raising high made by a capillary tube in the normal laboratory condition. It was found that distinct patterns were difficult to obtain for crystallization polymers and polymers with big shrinkage when temperatures change. Clear microstructures or patterns could be obtained by molding with amorphous polymers such as PS and PMMA.

Key words Micromolding, Polyethylene, Polypropylene, Polystyrene, Poly(methyl methacrylate)

1 Introduction

Producing micro-patterns on curved surfaces is one of the important requirements of microfabrication[1-3], like making micro-coil springs, coronary stents[4] and assembling micro-lens arrays on the surface of a lens[5]. The technology widely adopted in microfabrication is photolithography that produces microstructures accurately with, of course, some disadvantages. However, it is difficult to produce micropatterns on nonplanar surfaces by means of photolithography[6]; several procedures have to be taken to make multilevel microstructures. In addition, only a few materials could be used in photolithography [7] and the optical diffraction limits the sizes of the features. To overcome those shortcomings, several groups have developed a series of new micro fabrication methods known as soft lithography (SL)[8,9] including micro-contact printing (μCP)[10], replica molding (RM)[11], micro-transfer molding (μTM)[1,8,9], micro-molding in capillaries

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** 通讯联系人，E-mail：hpsm@ustc.edu.cn 收稿日期：2002-11-04；修回日期：2003-04-17.

(MIMIC)[12] and solvent assisted micromolding (SAMIM)[1,8,9]. The SL uses an elastomeric stamp that has microfeatures copied on the surface to transfer patterns during a printing or molding process. It is easy to operate without expensive equipment and suits to produce micropatterns with unconventional microfabrication materials such as polymers, ceramics and glass, and it is extended to biology[13], electronics[14] and many other high-tech fields. Since the stamp is made by organic silicon rubber with good elasticity, SL can produce microstructures on curved surfaces.

In this presentation we used the organic silicon rubber stamp to mold micropatterns with molten polymers directly. With the good elasticity of the organic silicon rubber, micropatterns could be produced on curved surfaces of most common thermoplastic polymers easily. The multilevel microstructures were generated in a double molding process as well.

2 Experimental

2.1 Materials

The polymers used were common thermoplastics in industry grade. They were low-density polyethylene (LDPE) 1F7B, Yanshan Petrochemical Co., China; polypropylene (PP) FY4012, Polyolefin Company, Singapore; polystyrene (PS) and polymethylmethacrylate (PMMA), Lanzhou Petrochemical Co., China. The organic silicon rubber of polydimethylsiloxane (PDMS, SDM-801) and the hardener were obtained from the Chenguang Institute of Chemical and Engineering, Sichuan, China. The glass masters with the micro-lines on the surface were produced by normal photolithography in the National Synchrotron Radiation Laboratory, the University of Science and Technology of China.

The thermal molding was performed on a thermo-platform controlled by a thermostat. The temperature was the apparent one measured on the surface of the platform.

2.2 Preparation of the elastomeric stamp

The key element in micro-molding is the elastomeric stamp. The compound used is the organic silicon rubber of polydimethylsiloxane (PDMS) (A) and the hardener (B) which were weighed as 100∶3 and mixed. The air bubbles were driven out of the mixture in vacuum, and then the mixture was cast onto the glass master like the schematic illustration in Fig. 1. Having cured for 8 h at the room temperature, the PDMS stamp was taken off carefully and the microstructures were copied onto the surface of the stamp.

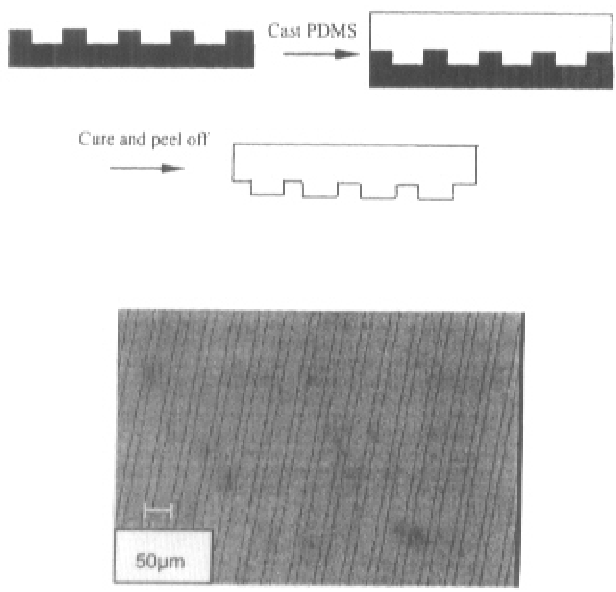


Fig. 1　Schematic illustration of the steps for preparing the PDMS stamp (upper one) and the microscopic photo of the PDMS stamp (underside)

2.3 Micromolding on the planar surface

The thermoplastics pellets and the elastomeric stamp were placed separately on two microscopic glass slides preheated at the pre-designed temperature (depending on their molten temperatures) on the thermo-platform. As soon as the thermoplastics pellets were melted, the stamp was pressed on the polymers with a force of 1N, and then they were taken off and cooled down to the room temperature in 2 min in the air. The microstructures on the stamp have now been transferred onto the surface of the plastics. Fig. 2 is the microscopic pictures of the LDPE, PMMA, PS and PP with micro-lines on them stamped at 150, 190, 180 and 190℃, respectively. The sharp lines can be seen for all polymers. Here the preheating of the stamp is indispensable. If the micro-molding was carried out without preheating the stamp, there might be some bubbles or holes on the surface of the polymer because the air adsorbed by the PDMS stamp surface would expand and go out when heated.

2.4 Micromolding on a curved surface

One of the advantages of micromolding is its ability to mold the micropatterns on a curved surface. In order to do so, a glass tube with an outer diameter of 7.4 mm was used to provide the curved surface. After the molten polymer was scraped onto the outer surface of the tube, the preheated stamp was pressed on it for 2 min. Fig. 3 is the LDPE micro-patterns on the curved surface of the tube. The clean sharp lines with a little curvature were obtained again.

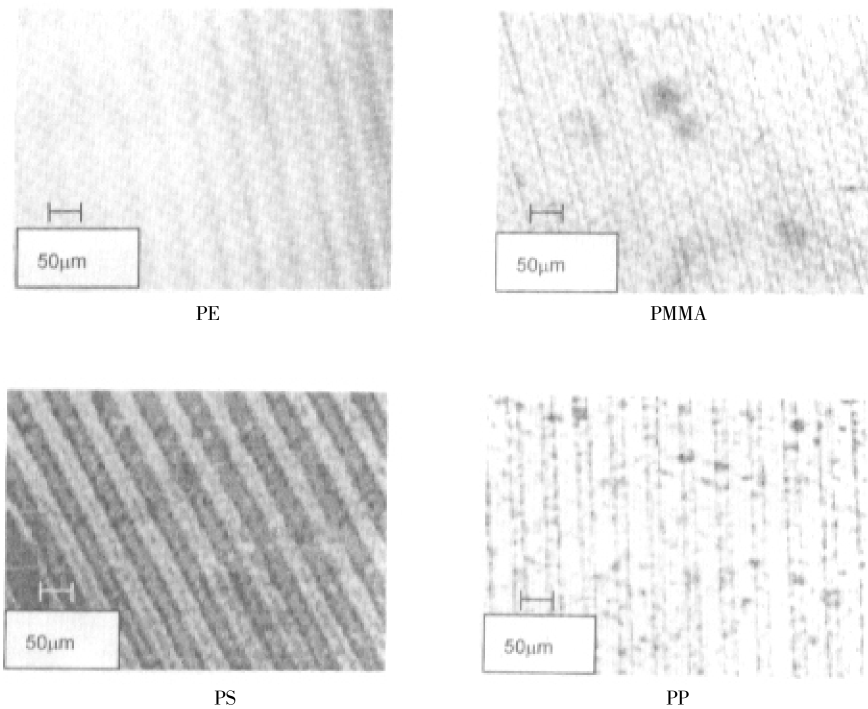


Fig. 2 Photos of microlines made by micromolding on four different thermoplastics

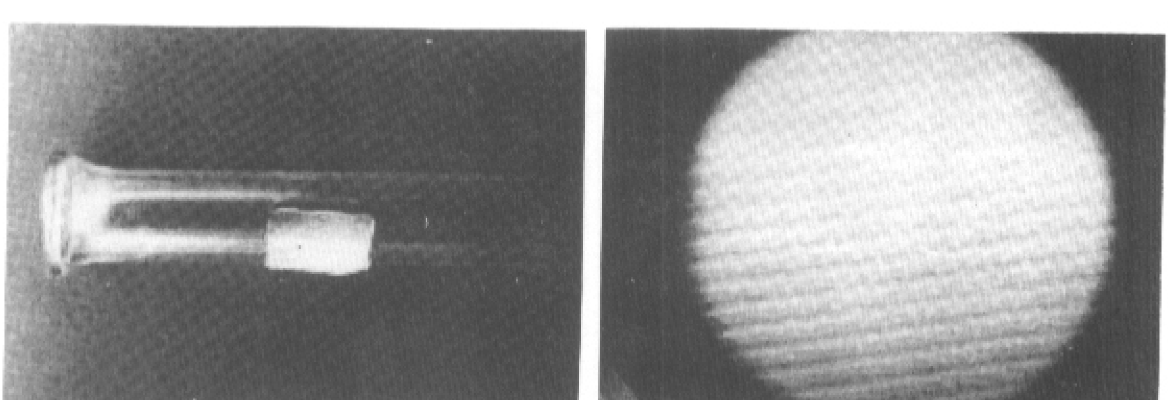


Fig. 3 LDPE micro-patterns were produced on the curved surface of a glass tube

For polymers, such as PS, with low fluidity at their molten temperatures, the sample must be made into a film on the tube first. After preheating, they were rolled on the stamp. Fig. 4 shows the microstructures on the PS surface produced by micromolding on the outer tube. It can be seen from the Fig. 4 that the curvature of the lines is obvious with brightness in the lower part of the figure and a little darker in the upper part of the figure.

2.5 Molding micro-stripes on micro-towers raised by a capillary

It is a big challenge to transfer the micropatterns onto the surfaces of smaller curvature[15]. Fortunately micromolding is able to do this task very well. To demonstrate it, a glass capillary with the diameter of 0.44 mm was placed on the glass substrate to form a miniraising high, and then micromolding was carried out on it with four polymers. It proved that micro-patterns could be produced even on the curved surface of curvatures of several millimeters by micromolding. The micropatterns produced in this way with four polymers of LDPE, PMMA, PS and PP were shown in Fig. 5. The column in every picture where there is capillary under the polymer films exhibits the clear lines, the same as the lines in the other parts of the picture. There are some coarse surfaces of PP microstructure due to the crystallization.

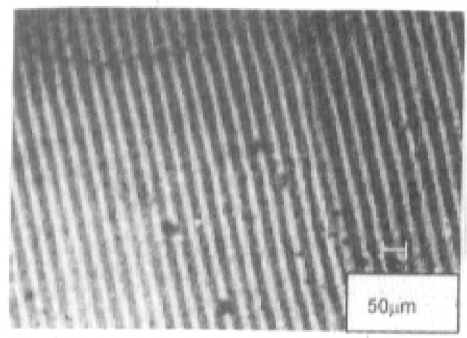
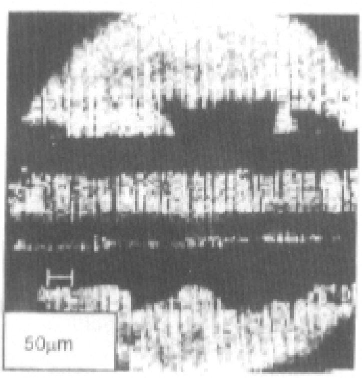
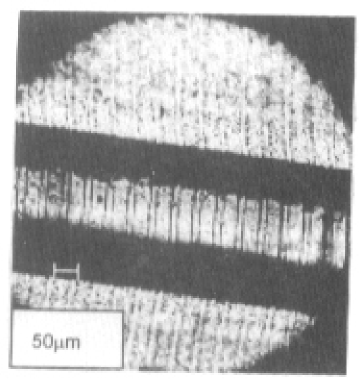


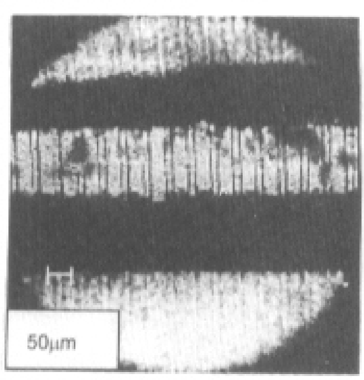
Fig. 4　Microstructures on the PS surface produced by micromolding on the outer tube



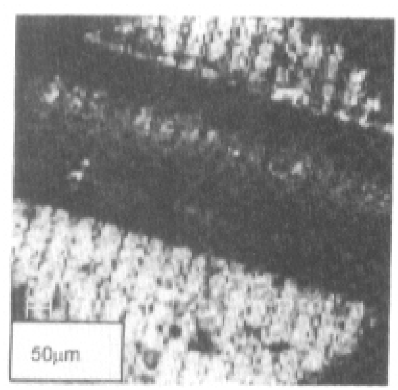
LDPE(150℃)



PMMA(190℃)



PS(180℃)



PP(190℃)

Fig. 5　Micropatterns produced with the thermoplastics of LDPE, PMMA, PS and PP on the surface with a raising high of capillary

3 Discussion

The micromolding here is molding microstructures on the common polymer surface directly instead of using polymer precursors [5,9,10]. Thus the micromolding here can produce microstructures more quickly. Because PDMS can keep its physical properties in a wide temperature range (−100 ~ 250℃) and is durable for oxidation[16], it can be used in the micromolding for most commercial thermoplastics. The elastomeric stamp is easy to produce and can be used up to 50 times in thermal micromolding. Most important is that the micromolding can be used to produce microstructures on curved surfaces and make multilevel microstructures.

Distinct patterns are difficult to obtain for crystallization polymers and polymers with big shrinkafe when temperatures change. For example, microstructures as small as 3 μm can't be made on the surface of crystalline polymers, and acetal copolymer POA. It is the amorphous polymers such as PS and PMMA that have a good possibility to mold the clear microstructures or patterns.

Compared with the photolithography, and as a new branch of soft lithography, the micromolding is simpler and more efficient. The micromolding requires an elastomeric stamp only and the printing process is quite simple, while photolithography involves complex procedures and expensive equipment.

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