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Compressed-CO_2-Assisted Patterning of Polymers

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We report a facile route to pattern polymer surfaces with the aid of compressed CO_2, termed the compressed-CO_2-assisted imprint method. In this method, compressed CO_2 serves as a plasticizer for polymers (such as poly(methyl methylate) and polystyrene), which leads to a tremendous reduction in the glass transition temperature and viscosity of the polymers. Nylon fabrics and anode aluminum oxide porous membranes are used as molds, respectively, to pattern the softened polymers at relatively low temperatures, resulting in patterns at the scale of micrometers and nanometers on the surface of polymer films. The patterned structures can be tuned by changing CO_2 pressure and temperature in the imprinting process. This method is simple and environmentally benign. It also can be operated at low temperatures, for instance, ambient temperature.

Introduction

Patterning has been extensively applied in various fields in modern science and technology.[1] Besides conventional lithography, many other patterning techniques, such as imprint lithography[2] and soft lithography,[3] have emerged in recent years. It is well-known that polymeric materials have been used in diverse fields, and special patterns of polymers are required in many cases. The imprint process for thermoplastic polymers using physical compression molding, featured as a low-cost mass-production technique, has been applied for decades as a routine method for fabricating patterns at a scale of micrometers and above. Recently, it was demonstrated that the imprint technique could also be able to mass-produce sub-10-nm structures, which was termed “nanoimprint lithography”.[4] In the imprint process, a prepatterned mold is pressed into a thermoplastic polymer film. In many cases, the polymer film is thermally softened at a temperature higher than the glass transition temperature (T_g) of the polymer ($T > 1.2T_g$) to attain enough fluidity and thereby can conform to the mold. This technique has some inherent drawbacks. For example, a high temperature is often required, which sometimes results in distortion of the imprinted structures and even the mold patterns after the heating−cooling cycle; moreover, it is not suitable for thermally sensitive polymers. In addition, antiadhesion agents have to be used to get a clean release of the polymer from the mold.[5]

Obviously, the methods for patterning polymers at relatively low temperatures are desirable, especially for pattering thermally degradable polymers.[6] Some researchers have carried out elegant related work. Lee et al. presented solvent-assisted room-temperature imprint lithography. In their approach, the polymer was allowed to absorb solvent vapor, and then, the swollen polymer was pressed at room temperature to complete the pattern transfer from mold.[6] Note that treatment to polymer with solvent to enable room temperature processing was first used in SAMIM, solvent-assisted microcontact molding;[7] some authors developed a more direct process, in which a polymer film was directly pressed by a mold at room temperature and very high pressure, typically about 30−150 MPa.[5] However, the above imprint methods suffer from some disadvantages. For the solvent-assisted imprint process, the degree of the plasticization of polymer cannot be controlled exactly. Thus, the patterning is not controllable. Moreover, it is difficult to remove the absorbed solvent from the polymer completely. If the imprint is performed below the T_g value of the polymer, extremely high pressure must be applied to achieve a full pattern transfer from the mold to the polymer, which readily leads to deformation of the mold and then deterioration of the replication precision.

In recent years, the interactions between compressed CO_2 and polymers have been studied extensively. Although most polymers are insoluble in compressed CO_2, they can absorb a large amount of CO_2, which has a plasticization effect to reduce the T_g values of many polymers significantly.[8,10] On the basis of the compressed-CO_2-induced polymer plasticization, many applications have been investigated, including the preparation of polymer blends[11,12] and inorganic/polymer nanocomposites,[13,14] impregnation of dyes[15] and pharmaceuticals and proteins,[16] foaming of polymer,[17,18] and low-temperature welding and bonding.[10,19]

In the present work, on the basis of the plasticization effect of CO_2 on polymers, we propose a compressed-CO_2-assisted route to pattern polymer films, termed the compressed-CO_2-assisted imprint method. In this method, compressed CO_2 served as a plasticizer for polymers, which led to a tremendous reduction in the T_g values and viscosities of the polymers. As a result, the softened polymer was patterned by different molds including nylon fabrics and anode aluminum oxide (AAO) porous membranes under a slight press (e.g, a weight of 200 g used in this work) at low temperatures. The patterned film was obtained after releasing CO_2 and removing the mold. The effects of pressure and temperature on the surface patterns were investigated systematically. It was found that a mold pattern can be faithfully transferred to the polymer in a controllable way by tuning the temperature and pressure of CO_2.

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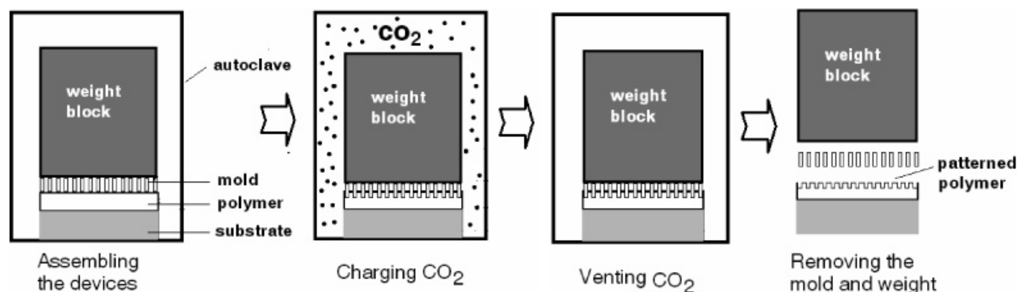

Figure 1. Schematic diagram of the compressed-CO_2-assisted imprint process.

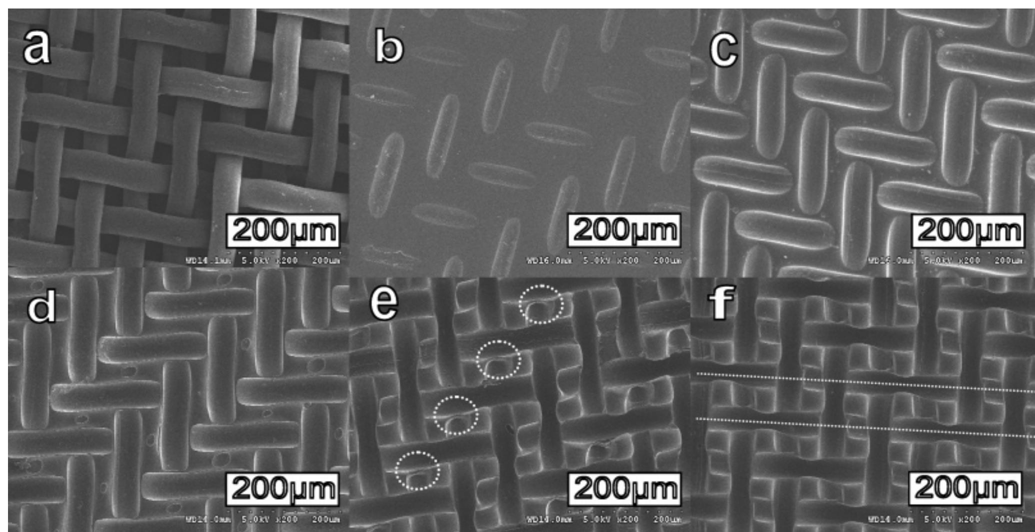

Figure 2. SEM images of (a) the nylon fabric mold and the patterns on PMMA film imprinted at (b) 35 °C and 4 MPa, (c) 50 °C and 4 MPa, (d) 35 °C and 7 MPa, (e) 35 °C and 10 MPa, and (f) 35 °C and 15 MPa.

Experimental Section

Materials. Filter fabrics (350 mesh) weaved from 50-μm-diameter nylon fibers, purchased from a local market, were used as the molds after being ultrasonically washed in acetone and dried in the air. AAO porous membranes, provided by Watman, were directly employed as the molds. Our SEM observation showed that the pore diameter of the membranes was about 250 nm. The polymer materials, including PS (M_w = 27 4370, M_n = 91 230), PMMA (M_w = 103 700, M_n = 37 800), and other reagents, are all commercially available and used without further purification. Solvent cast polymer films were obtained from 10−15 wt % toluene−polymer solution and baked in a vacuum to remove the residual solvent before use. Carbon dioxide with a purity of 99.95% was provided by Beijing Analytical Instrument Factory and used as received.

Procedures to Pattern the Polymer Film. Figure 1 shows a schematic diagram of the procedures for patterning the polymer film with the aid of compressed CO_2. Typically, in a stainless steel autoclave, the mold (~1 cm × 1 cm nylon fabrics or AAO membrane with a diameter of 1.3 cm) was first placed on an ~1.5 cm × 1.5 cm piece of polymer film mounted on a glass substrate; then, a 200 g cylindrical weight block was pressed onto the mold. After being sealed, the autoclave was immersed in a water bath of a desired temperature. The air in the autoclave was replaced with CO_2, and more CO_2 was charged up to a desired pressure using a DB-80 high-pressure syringe pump. The system was maintained at this condition for 60 min, and then, CO_2 was released slowly at room temperature. The nylon fabric mold could be removed easily from the polymer. The AAO membrane mold was removed by dissolution with 6 M HNO_3 aqueous solution overnight.

Characterization. The patterned films were examined under a Hitachi-S4300 scanning electron microscope operated at 5.0 keV. Samples were spray-coated with a thin layer of platinum before observation.

Results and Discussion

In this work, nylon fabrics and AAO film were used as molds to pattern different polymers with the aid of compressed CO_2, respectively. In the case of nylon fabrics as mold, patterns of micrometer scale were obtained, and the effects of pressure and temperature on patterning polymer were investigated in detail. With the AAO film as mold, nanometer patterns were produced on the surface of the polymer.

Nylon Fabrics as Mold to Pattern the Polymer Surface. Figure 2 shows the patterns on PMMA films fabricated using nylon fabrics as mold in compressed CO_2 at different temperatures and pressures.

As shown in Figure 2a, the mold is composed of perpendicular longitudinal and latitudinal fibers with a smooth surface, and these fibers possess a uniform diameter of 50 μm and a round cross section. When PMMA film was imprinted with this mold in CO_2 at 1 MPa and 35 °C, no detectable pattern could be found on the film under SEM observation. The reason for the failure of the patterning is that the polymer cannot be efficiently plasticized because a smaller amount of CO_2 is dissolved under these conditions.[8] When the pressure increased to 4 MPa at 35 °C, arrays of shallow pits on the surface of the PMMA film (Figure 2b) can be observed, which resulted from the compression of the protruded section of the fibers in the mold onto the partially plasticized PMMA film. At 4 MPa and 50 °C, clear arrays of pits with a larger size appear on the

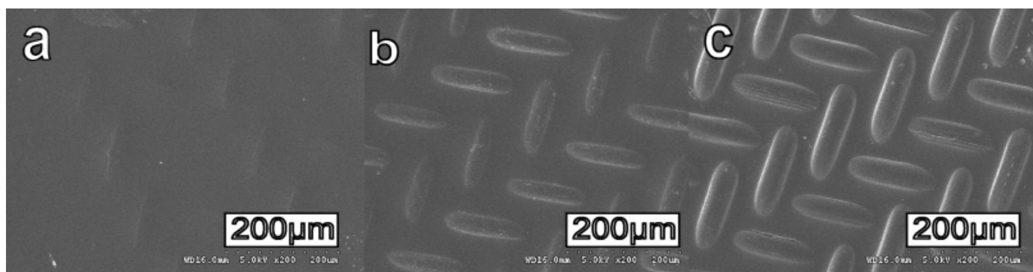

Figure 3. SEM images of surface patterns on PS films imprinted at 35 °C and different pressures of (a) 4 MPa, (b) 7 MPa, and (c) 15 MPa.

surfaces of the PMMA film (Figure 2c). This is easy to understand because the polymer is more easily plasticized with CO_2 at the higher temperature.

The effect of pressure on the patterns of the PMMA film surface was studied systematically at 35 °C, and the SEM images of the patterns imprinted at 7, 10, and 15 MPa are shown in parts d, e, and f of Figure 2, respectively. The general trend is that the penetration of mold into substrate becomes deeper under the press of the same weight (200 g) with increasing CO_2 pressure, because the degree of plasticization of the polymer becomes larger due to the larger solubility of CO_2 in polymer at higher pressures.[20] Compared with the pattern imprinted at 4 MPa (Figure 2b), the size of the features on the pattern generated at 7 MPa enlarges to three dimensions; that is, the length, width, and deepness of the pits on the polymer surface simultaneously grow. From Figure 2d, we can see that there are two kinds of pits oriented at perpendicular directions, originated from longitudinal and latitudinal fibers, respectively, and each pit almost contacts all of its four closest neighboring pits. Comparatively, the pit arrays in Figure 2b are much sparser, and they separate from each other with a larger space. In addition, the diameter of the pits in Figure 2d is very close to that of the fibers in the nylon mold, indicating that nearly half of the cross section of the mold fiber is inserted into the polymer film at 7 MPa. At 10 and 15 MPa (Figure 2e and f), the pattern pits are even longer and deeper, and the pits aligned at different directions tend to cross and bring new dotlike patterns. At a pressure of 10 MPa, the crossing of these pits is not in a complete way, and there are some parts left untouched by the mold fibers (see the circles in Figure 2e). However, in Figure 2f, the pits at different directions cross entirely and the pits oriented at the same direction almost form a continuous channel (see the line in Figure 2f).

It is known that many polymers can be effectively plasticized by CO_2. In this work, we also patterned PS films using this method, and some SEM images of the surface patterns imprinted at 35 °C and different pressures are given in Figure 3. Obviously, there is also a trend of enlarged size of patterned pits with increasing CO_2 pressure. In addition, compared with the patterned PMMA films imprinted at the same pressure and temperature, the pits on PS films are shallower and the distance between the features is longer. For example, at 35 °C and 4 MPa, a noticeable pattern can be achieved on PMMA film, while there is no detectable pattern on PS film under the same conditions. This phenomenon is mainly attributed to the weaker interaction between CO_2 and PS; that is, the degree of plasticization of PMMA is larger than that of PS under the same pressure.[8]

AAO Film as Mold to Pattern the Polymer Surface. In all of the imprint processes above, the nylon fabric with patterns at the scale of micrometer was used as the mold. It is expected to extend such a compressed-CO_2-assisted imprint method to the scale of nanometers. We adopted AAO membrane with a denoted pore diameter of 100 nm as the mold to explore the possibility of nanoscale patterning. With the porous AAO membrane as the mold, brushlike patterns on PMMA films were obtained under different conditions, as shown in Figure 4. More importantly, the length and therefore the aspect ratio of the brush hairs could be finely tuned by changing the CO_2 pressure. For example, at 35 °C and 5 MPa, the length of the resulting surface hairs was about 200 nm (Figure 4a), while the hair length was approximately 500 nm when the CO_2 pressure was increased to 7 MPa. With further increase of the CO_2 pressure to 15 MPa, surface hairs with a length over 1.5 μm were obtained (Figure 4c). From parts a to c of Figure 4, the length of the brush hairs steadily increased with the rise of the pressure at the same temperature. This growth of the brush hairs with pressure can also be explained by the continuous enhancement of the plasticization of the polymer. Note that, in most cases, there is a meniscus at the protruding end of the brush hairs (highlighted with arrows in Figure 4a), indicating that the brushlike pattern was formed by wetting of the mold pores of the plasticized polymer driven by the capillary force, which is similar to that in the capillary force lithography method.[21,22] In addition, when the imprint process was carried out at 75 °C and 19.0 MPa, we could get dense fibers with a very large aspect ratio on the polymer surface after the removal of the mold (Figure 4d).

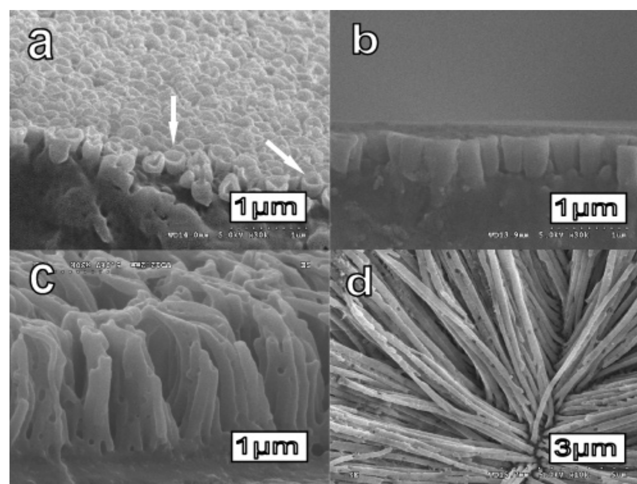

Figure 4. SEM images of brushlike pattern on PMMA films imprinted with AAO membrane mold at various CO_2 pressures and temperatures: (a) 35 °C and 5 MPa; (b) 35 °C and 7 MPa; (c) 35 °C and 15 MPa; (d) 75 °C and 19 MPa.

Conclusion

In summary, based on the effective plasticization effect of compressed CO_2 on polymers, we developed a compressed-CO_2-assisted imprint method, which could be applied to imprint polymer films and endow both microscale and nanoscale patterns. This route has some unique advantages: it is environmentally benign; it only requires a low operation temperature

(e.g., ambient temperature), and easy control of the structure of the patterns is possible by tuning the CO_2 pressure. We believe that this method can be widely used for the patterning of many polymer materials.

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