Micropatterned Polymer Films by Vapor-Induced Phase Separation Using Permeable Molds

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ABSTRACT Microstructured polymeric films are fabricated by a novel replication method. A polymer solution is applied and contained between two substrates, of which at least one is a patterned PDMS mold. The ensemble is then put in an atmosphere containing water vapor, which diffuses through the PDMS. The absorption of water into the polymer solution causes the precipitation (phase separation) of the polymer while in contact with the microstructured molds. The thickness of the PDMS slab can be exploited to tune the water vapor transport and hence the phase separation kinetics and resulting polymer morphology. Removal of excess polymer solution from between two PDMS slabs, followed by vapor induced phase separation, can also result in microperforated polymer films with great control over the dimensions.

KEYWORDS: Porous polymeric film • patterning • phase separation • PDMS • replication

INTRODUCTION

Phase separation processes are among the most widely used today for the production of porous polymeric films (1). In these processes, a polymer solution is forced to separate into two phases with significant differences in polymer concentration. The polymer-rich phase solidifies, creating the matrix of the film. The polymer-lean phase forms the pores of the film. The phase separation can be induced in many ways, but the most common ones are a change in temperature or the addition of a nonsolvent to the polymer solution.

The addition of a nonsolvent modifies the composition of the system. An extra component is present that is fully miscible with the solvent but does not dissolve the polymer. When a certain composition is reached, the phase separation proceeds. The nonsolvent can be added in its liquid state by immersing a polymer solution cast on a substrate into a coagulation bath. This is the so-called liquid-induced phase separation (LIPS). Another way of contacting the polymer solution with the nonsolvent is by letting the vapor of the latter flow over the polymer solution, which will absorb it. This process is known as vapor-induced phase separation (VIPS). VIPS is a rather common process normally used for obtaining membranes with larger pores at the top surface (2).

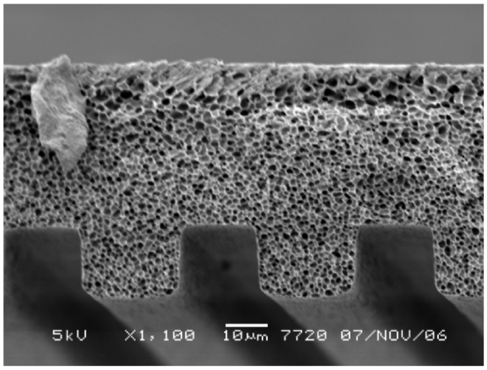

FIGURE 1. Membrane with a line pattern made from PES. This film was obtained through PSμM of an NMP solution in water, using a silicon wafer as a mold. The phase separation has initiated from the flat side in this case.

Phase separation micromolding (PSμM) was introduced a few years ago (3). This microfabrication method comprises the casting of a polymer solution onto a structured silicon wafer, followed by phase separation of the polymer solution. In this way, structured porous polymeric films were obtained (Figure 1). This process has been successfully used in combination with LIPS and VIPS and has yielded microfluidic devices (4), tissue scaffolds (5), microsieves (6), and porous molds for microcontact printing (7). The inherent shrinkage of the process facilitates the release from the mold, rendering defect-free replicas. The downside is that it can also deform the replicas of the features (8).

Another common disadvantage in play with PSμM is that the phase separation is always induced from the nonstructured side (i.e., the side that is not in contact with the mold and is open to the coagulating agents). The coagulation front moves through the film, often creating a hierarchal pore size gradient. As the nonsolvent diffuses into the polymer solution, it drags along solvent with it. This creates a variation in local concentrations of nonsolvent across the membrane, leading to pore size differences. The pore size decreases toward the side originally in contact with the coagulation bath. Often, a dense skin is formed on this interface. As a

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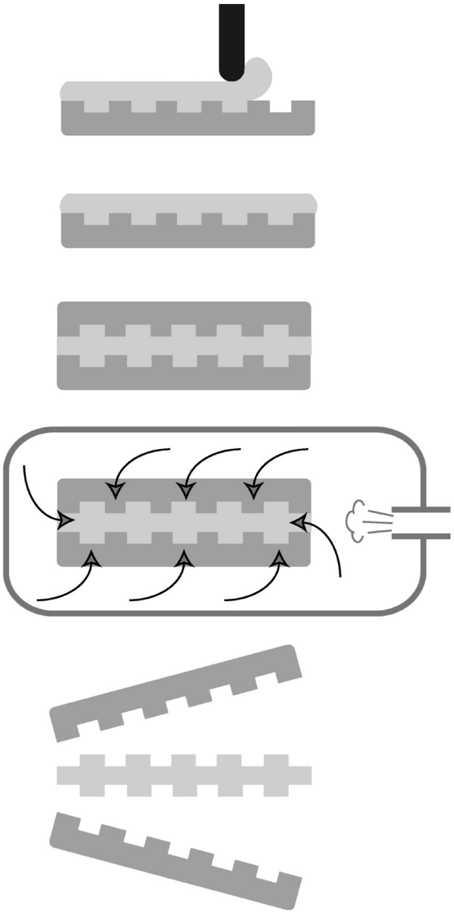

FIGURE 2. Vapor-induced phase separation using two permeable molds. In this case, the polymer solution is cast onto a flexible, permeable PDMS mold. A second mold is then put on top of the solution. The ensemble is introduced in a water vapor atmosphere. Upon phase separation, a bistructured membrane can be obtained.

result, the selective layer of a membrane is located on the unstructured side.

In this work, we introduce flexible PDMS molds on nonwoven supports for use in vapor-induced phase separation micromolding (VIPSμM), illustrated in Figure 2. The high permeability for nonsolvent vapor of PDMS makes it an ideal mold material. To the best of our knowledge, this is the first time PDMS is used as a permeable mold that allows the addition of a nonsolvent to a polymer solution, yielding (also as a first) bistructured porous polymeric films.

EXPERIMENTAL SECTION

PDMS Mold Preparation. SU-8 (Microchem) was used to create the master from which the PDMS molds were replicated. SU-8 is an epoxy based negative resist that is sensitive to ultraviolet radiation. Silicon wafers with SU-8 structures with the desired features were prepared in cleanroom facilities. Where needed, multiple layers of SU-8 were processed. Subsequently, the wafers were hydrophobized through contact with trichloroperfluorooctylsilane vapor (FOTS, Aldrich Chemicals) at 120 °C for 2 h, and then cooled to room temperature and heated again to 100 °C for 1 h.

A 10:1 Poly (dimethylsiloxane) (PDMS, Silicone RTV 615 A/B, General Electric) pre-polymer-cross-linking agent mixture was degassed for 0.5 h and cast onto the hydrophobized wafer. After 15 min at 60 °C, a polyethylene nonwoven support layer was put on top of the liquid. The PDMS was then allowed to cure for a total of 4 h at 60 °C.

Materials and Solution Preparation. Two polymer solutions were used in these experiments. The first one was made of Polyethersulfone (PES, Ultrason, E6020P) in a concentration of 15 wt % in N-methylpyrrolidone (NMP, 99%, Acros Organics). Polyvinylpyrrolidone (PVP K30, Fluka) was added to the solution. PVP is commonly used to create a percolating porosity and a hydrophilic surface (9). It also acts as a macrovoid formation inhibitor (10). Its concentration was 5 wt %.

The second solution was made by dissolving poly (L-lactic acid) in a concentration of 10 wt % (PLLA, kindly provided by D. Grijpma, Department of Polymer Chemistry and Biomaterials, University of Twente) in dioxane (Merck, analytical quality). This solution has only been used for the experiment depicted in Figure 5.

Tap water vapor was used as nonsolvent. All reagents were used as received, without further purification. Unless otherwise specified, solutions were prepared by weighing all the components into a plastic bottle and left on a rolling bank until complete dissolution.

Membrane Fabrication. The polymer solution was always administered with the help of a pipet and cast with casting knives of different heights. If a flat glass plate or a silicon wafer were used, the polymer solution was cast onto them and the PDMS mold was later laid onto the liquid layer. If both sides were structured with PDMS molds, a bit of polymer solution was cast onto both molds, which were then brought in contact and pressed lightly with a roller. For perforated membranes, the molds were pressed against each other with the help of a lamination machine.

When the ensemble was ready, it was suspended in a pot above the surface of boiling water. The pot was covered with its lid, which possessed a small hole for purging. In this way, an environment of pure water vapor (air free, thus not 100% relative humidity, but 100% water vapor) could be created for the coagulation of the membranes, which usually took less than 10 min.

Membrane Treatment and Inspection. Membranes were rinsed with water overnight and broken in liquid nitrogen when needed for cross-section pictures or cut with a scalpel for surface pictures.

Prior to SEM inspection (Jeol JSM 5600LV), the membranes were dried overnight under a vacuum at 30 °C and then sputtered with gold (Balzers Union SCD040).

RESULTS AND DISCUSSION

VIPS through PDMS. Inducing phase separation in a polymer solution with vapor requires a sustained and significant flow of this vapor into the solution. This is the reason why the mold material should present very high water permeability. Table 1 shows a list of water vapor permeability values for common polymers. It can be observed that PDMS is indeed highly open for water transport.

PDMS is a readily accessible material and as it can be acquired as a curable liquid, it can be molded in a very easy way. It is mechanically and chemically stable and according to our experiments does not swell extensively when in contact with NMP (very common solvent for polymer solutions). All these characteristics make it the ideal candidate for molding in our systems. The layers in use were usually around 100 μm thick. To ease handling, we introduced a layer of a nonwoven support at the unstructured side early during the curing process. In this way, a more robust film was obtained.

Table 1. Water Vapor Permeability for Various Polymers at 30°C, Extrapolated to 0 Water Vapor Activity

polymer	abbreviation	H_2O permeability (barrier = 7.5 × 10^{-18} m^2 s^{-1} Pa)	ref
polyamide 6 (Nylon 6)	PA-6	275	(15)
polyacrylonitrile	PAN	300	(15)
polyimide (Kapton)	PI	640	(16)
polyethersulfone	PES	2620	(15)
sulfonated polyethersulofone	SPES	15000	(17)
polydimethylsiloxane	PDMS	40000	(18)
sulfonated polyetheretherketone	SPEEK	61000	(19)
$1000_{PEO}56_{PBT}44$	PEO-PBT	85500	(20)

PDMS controls the vapor transport during the VIPS process. We have carried out experiments to help us assess its effect on the final morphology of the film. These experiments involved the casting of a 100 μm thick layer of polymer solution on a smooth glass plate and covering it with a smooth PDMS film (100 or 300 μm thick). Figure 3 shows the effect of the PDMS layers on the porous morphology of the cross-section of the polymeric film. As can be seen, a layer of 100 μm of PDMS does not cause significant changes on the cross-section of the membrane compared to an uncovered film. The 300 μm layer of PDMS causes a noticeable growth of the pores.

Work on poly (ether imide) membranes formed from an NMP solution through VIPS with water vapor show a similar behavior when the amount of vapor in the coagulation atmosphere is lowered. The size of the cells decreases with increasing relative humidity (11). Furthermore, cellular structures are only obtained when the relative humidity of the vapor bath is above 27%. It seems that this affects the position where the binodal is entered and how fast this is done (12).

Having observed that PDMS is a suitable material for controlling water vapor permeation, we have made different molds. Following the methods described in the experimental section, multiple structures can be created with PDMS. See Figure 4 for different examples of molds with lines or pillars. The introduction of gutters to facilitate the distribution of the excess of polymer solution is also shown.

Replication from Permeable Molds. Figure 5 depicts two membranes with line patterns and the flexible mold used to obtain them. In the top case, the polymer solution was applied on a glass plate. After casting with a knife, a PDMS mold with a line pattern (inlay in the middle the figure) was laid on it. The replication of the features is successful, with no disagreement in dimensions between mold and membrane. In the bottom case, the PLLA solution was contained between two PMDS molds. Shrinkage related phenomena as observed with solid silicon molds is not observed here (13).

The same experiment was carried out using a PDMS mold with pillars of different shapes. Figure 6 shows the replication of pillars in the shape of a star and a heptagon. In the picture presented here, the structures are replicated perfectly. These features would suffer from shrinkage in regular phase separation microfabrication. The bottom picture in

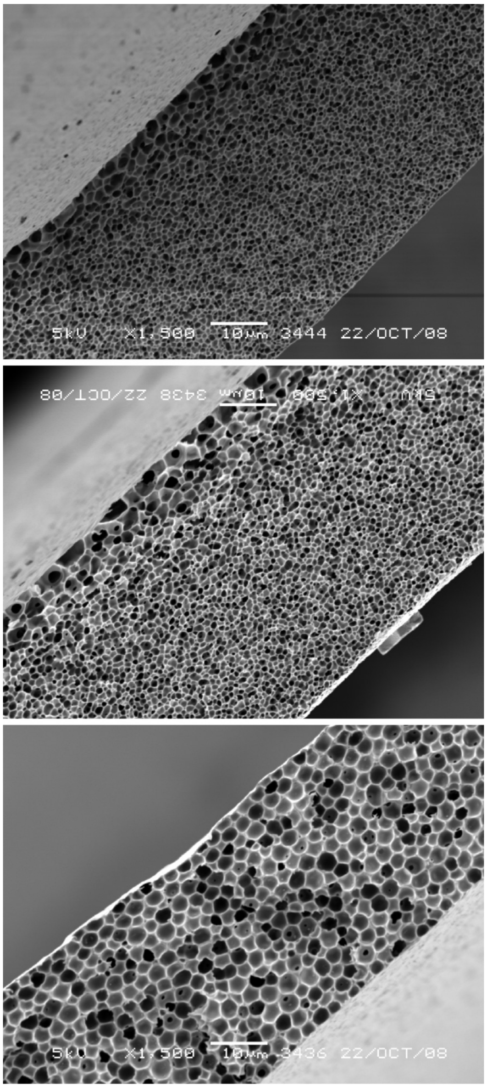

FIGURE 3. Effect of PDMS thickness on final porous morphology. The pictures at the top (no PDMS) and middle (100 μm PDMS) present no major differences in morphology. In contrast, the picture at the bottom (300 μm PDMS) shows bigger cells in the cross-section, compatible with slower phase-separation processes.

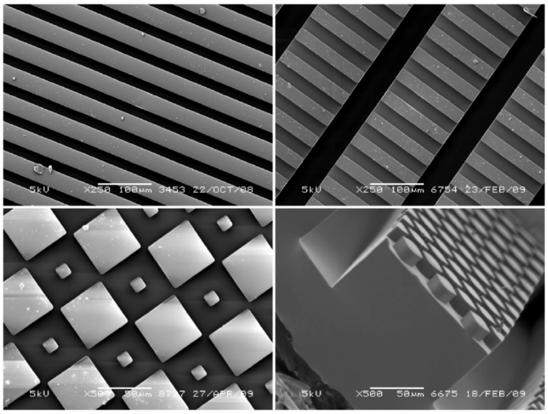

FIGURE 4. Examples of PDMS molds. The pictures on the top show line patterns. The pictures on the bottom show pillars. The molds on the right side possess gutters, which divide the pattern periodically.

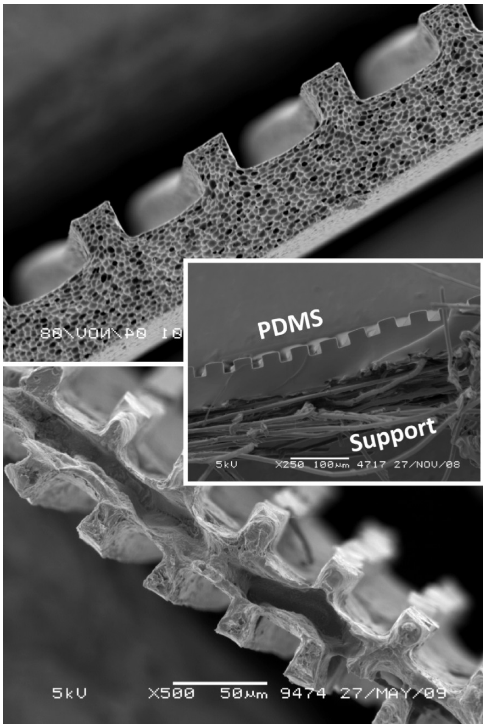

FIGURE 5. Top: PES membrane obtained by phase separating a polymer solution contained between a glass plate and the PDMS mold shown in the middle. Bottom: PLLA membrane obtained by using two of these molds. The dimension of the features in both membranes and molds are in good agreement and no noticeable shrinkage is detected.

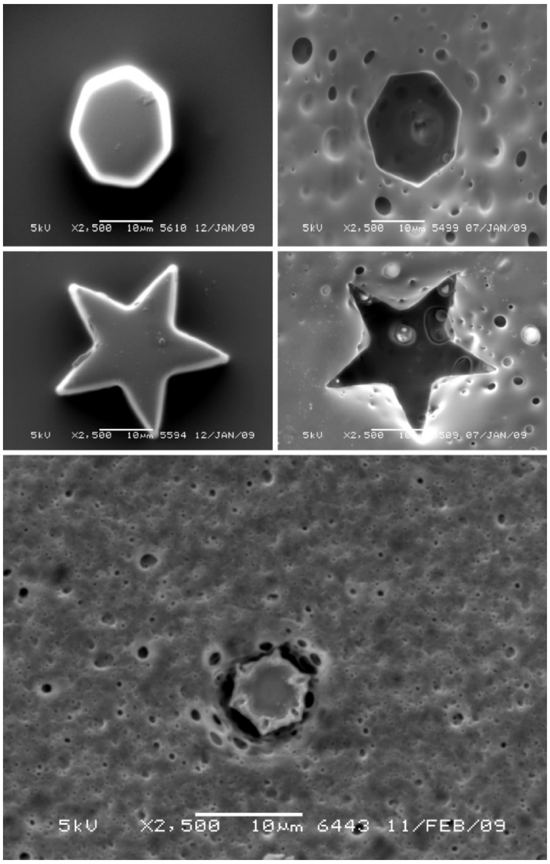

FIGURE 6. Top four pictures: Different pillars on a PDMS mold on the left side and their replicas on membranes on the right side. The features are replicated, with excellent agreement both in size and in shape. Bottom: Lack of fidelity in the replication of a hexagonal pillar in regular PSμM. It can be seen that the polymer retracts from the pillar, rendering a circular pore.

Figure 6 shows the lack of fidelity in the replication of a hexagon via regular PSμM, resulting in rounded corners. This phenomenon is not observed here, where the star in the membrane matches the star on the mold with excellent agreement. A reason for this could be that the polymer solution begins to solidify at the layer containing the features. The walls of the features themselves are the first ones to solidify. In other words, in VIPSμM through PDMS the nonsolvent comes from the structured side. This is not the case in regular PSμM.

This effect can be notoriously seen in Figure 7. This membrane was obtained through phase separation of a membrane contained between a silicon wafer (left side in the figure) and a PDMS mold (right side), both containing line patterns. The agreement between the membrane and the mold on the PDMS side is again remarkable. This is the first layer to solidify upon contact with vapor. The nonsolvent cannot penetrate through the silicon wafer. The features on the left side are rounded even though the mold is sharp edged. This layer is the last one to solidify. The nonsolvent required comes through the PDMS mold and diffusing through the solidified polymer solution in between. Shrinkage plays, therefore, a major role. An interesting phenomenon is the deformation of the pores on the PDMS side, required to comply with the confinement of the mold. This is not observed on the silicon side.

The advantages of using PDMS molds regarding shrinkage can be exploited on both sides of a membrane by replacing the silicon wafer mentioned before with another PDMS mold. The vapor can, in this case, enter from both sides. Figure 8 shows a membrane obtained using said configuration. This membrane shows well-replicated structures on both sides, with comparable size. An added advantage to this type of arrangement is the shortening of coagulation times, because of water diffusion from both surfaces of the membrane.

Perforated Membranes. The arrangement of pores with well-defined size and ordering is desirable for different applications (1). The so-called microsieves present this functionality. While there are inorganic microsieves made of silicon nitride, polymeric microsieves present many advantages. Polymeric microsieves are more flexible, less brittle (14), and cheaper to produce.

Gironès et al. have shown the use of PSμM to make polymeric microsieves (6). The solution is cast onto a silicon wafer containing pillars with size corresponding to the desired pore diameter. Upon solidification and release, a perforated membrane is obtained. This method is straightforward and relatively simple. The shrinkage phenomena taking place on the horizontal direction can cause some deformation on the pores, through stretching of the polymer against the pillars. This complicates the release from the mold. Furthermore, the silicon molds are quite sensitive toward damaging during the process.

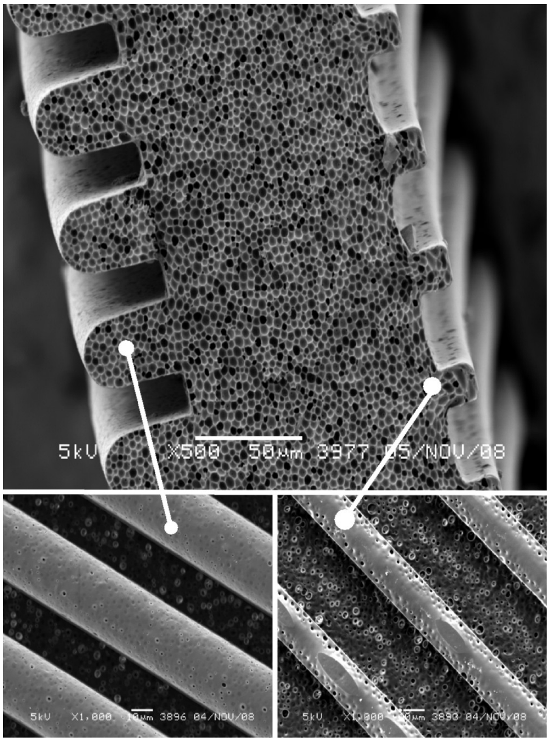

FIGURE 7. Bistructured membrane obtained using a silicon wafer (causing the structure on the left side, surface view on bottom left corner) and a PDMS wafer (causing the structure on the right side, surface view on bottom right corner). The PDMS side shows no shrinkage when compared to the mold, whereas the silicon wafer side shows noticeable roundedness of the features.

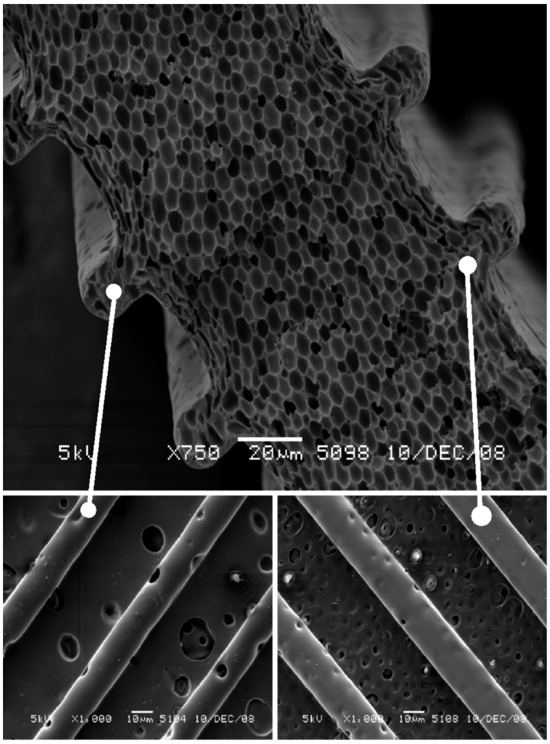

FIGURE 8. Micropatterned porous polymer film. The film was obtained by placing the polymer solution between two PDMS molds followed by vapor-induced phase separation with water permeating through the PDMS molds.

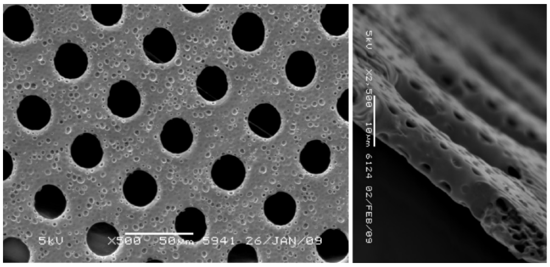

FIGURE 9. Polymeric microsieve obtained by using a PDMS mold with pillars and a smooth PDMS slab. The polymer solution was cast onto the smooth slab and the covered with the PDMS mold. The ensemble was put under pressure to ensure contact between the top of the pillars and the slab. The final porous polymer film is obtained after placing the stack in water vapor.

We have fabricated microsieves by using VIPSμM with PDMS molds. For this, the polymer solution was cast onto a smooth PDMS slab with no structures. Afterward, the solution was covered with another PDMS mold consisting of pillar fields. The ensemble was pressed together to ensure that the top of the pillars would touch the smooth PDMS layer. In this way, the excess polymer was pushed away. The ensemble was then put in water vapor environment to induce the phase separation. Figure 9 presents a microsieve obtained using this method, with a pore diameter of about 25 μm and a membrane thickness of 8 μm. The pores are separated 50 μm from each other. The mold in question presented pillars of 20 μm in diameter, about 15 μm in height and located 50 μm from each other.

The size of the pores is about 25% bigger than the diameter of the pillars. This can be the effect of squeezing the pillars. Also, the membrane is much thinner than the height of the pillars. Shrinkage of the polymer solution can be responsible for this disagreement.

In another approach, we have tried using two PDMS molds containing a line pattern but rotating one of the molds 90° with respect to the other. By doing this, the polymer solution was allowed to fill the lines on both molds, leaving gaps where the two molds touch each other. The molds were pressed together to squeeze out the excess of polymer solution. Figure 10 shows a good example of a microfence with square pores of 20 μm. As can be seen, the structure is well-defined. The fabrication method does not rely on perforation and the mold does not contain pillars. This allows for durable molds, easy processing, and trouble-free release. Figure 10 also shows that the filtration of polymeric beads is possible with these filters.

A disadvantage of the process is the lack of homogeneity in distributing the polymer solution by pressing the two molds against one another. Isolated thicker regions can be easily spotted on the newly formed membrane once it is peeled off the mold. In an effort to overcome this challenge, we have designed molds with gutters of increased depth, located every 100 μm. The result was a great improvement in the homogeneity of the membrane.

CONCLUSIONS

Phase separation microfabrication is a versatile tool for microstructuring porous polymeric films for a variety of uses. This process entails the phase separation of a polymer solution while it is in contact with a microstructured mold.

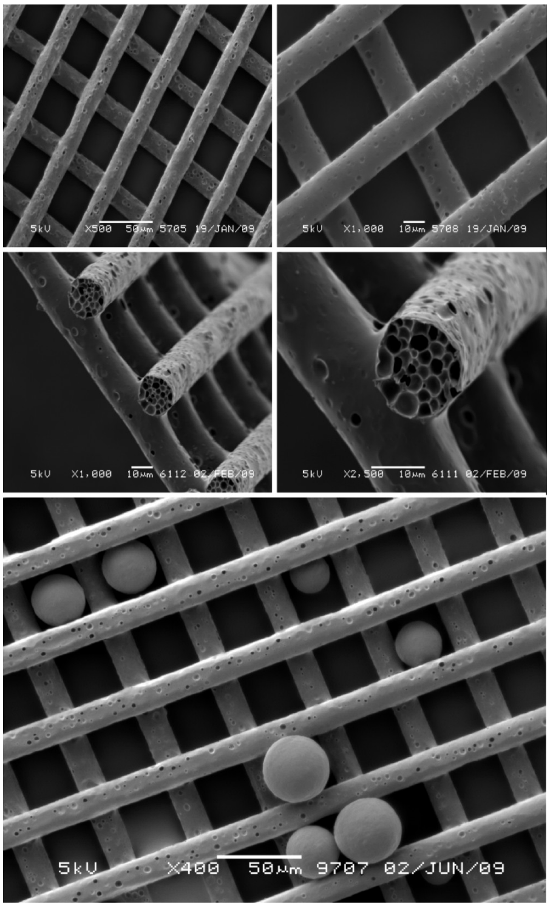

FIGURE 10. Sieving microfence obtained using two PDMS molds with line patterns, rotated 90°. The holes in the fence correspond to the locations where the ridges on both molds came into contact. The lines were made up by the valleys in the mold, which were filled with polymer solution. The sides of the square holes are about 20 μm.

In this case, we have shown that the use of PDMS makes for flexible, permeable molds. This is of high importance for a better replication of the structures. The opportunity to start the solidification process from the structured size guarantees that the features are extremely well replicated. Their structure is fixed and the layers of solution underneath them will not have an effect on them. This is not the case for PSμM on silicon wafers, as these are impermeable.

The use of permeable molds on both sides of the polymer solution allows for membranes with structures on both sides. Furthermore, pressing these molds against one another creates mold contact regions where no polymer solution is present. Upon solidification, these voids become pores through the film.

Using this phenomenon and two molds containing line patterns, we made microfences. These fences present an arrange of square pores produced without need for perforation by the mold, simplifying the process of microsieve making.

PDMS is a widely known material, structured through multiple methods. Its inclusion in PSμM extends the accessibility of this technique. In this way, the molding of polymers through phase separation can be implemented by researchers with considerable simplicity. Furthermore, no cleanroom facilities are required.

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