The use of high glass temperature polymers in the production of transparent, structured surfaces using nanoimprint lithography

Christopher A. Mills, Javier G. Fernandez, Abdelhamid Errachid and Josep Samitier*

Institute of Bioengineering of Catalunya (IBEC) and Networking Research Centre on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), Laboratory of Nanobioengineering, Barcelona Science Park, Josep Samitier 1-5, 08028 Barcelona, Spain.

Tel: (+34) 93 40 37 185, Fax: (+34) 93 40 37 181,

Corresponding author: *e-mail: cmills@pcb.ub.es, Fax: (+34) 93 40 37 181

Abstract

Polymers with high glass transition temperatures, fluorinated ethylene propylene copolymer (FEP) and poly(ethylene naphthalate) (PEN), have been used in imprint lithography as a protective support layer and as a secondary mould, to imprint superficial structures into a polymer with a lower glass transition temperature, namely poly(methyl methacrylate) (PMMA). As a support layer, FEP replaces fragile silicon based supports for the production of freestanding, structured sheets of PMMA, useful, for example, in biomedical applications where transmittance optical microscopy is required. Secondary PEN moulds, produced by imprinting using silicon-based primary moulds, have been used to transfer sub-micrometer tall structures to a freestanding PMMA sheet. Similarly, hole structures, with different dimensions, have been embossed in both sides of a PMMA sheet simultaneously.

Keywords: Polymer Engineering, embossing, nanoimprint lithography.

1 Introduction

Plastics and polymers have become increasingly utilised, in the decades since their discovery, as a rich source of experimental materials. In academia, and especially in the biological sciences, development of polymer based apparatus, such as lab-on-a-chip devices [1] or biochips [2], continues apace. The unique properties of plastics, such as strength, transparency and deformability, allied to simple manufacturing techniques and low cost, means they can be used as an alternative to their inorganic counterparts, such as metals or glass [3].

Polymer replication techniques, such as nanoimprint lithography (NIL), offer the ability to produce structures in polymers quickly and cheaply, and are scaleable for mass production. The method for NIL replica production has been outlined previously [4]. A number of replicas can be made through the utilisation of a single imprinting mould [5], which normally tend to be fabricated from metals or silicon-based materials [4], each of which has advantages. Unfortunately, the application of high pressures and temperatures will eventually produce defects in these inorganic moulds. These defects will degrade pattern quality and eventually cause the mould to fail. Therefore, it is important to investigate ways of extending the lifetime, or increasing the productivity, of a potentially expensive mould.

One way of doing this, recently described in the literature [6], is to use this more expensive, inorganic “primary” master mould to produce a rigid, polymeric “secondary” mould in a polymer with a high glass transition temperature (T_g). The secondary mould can be used to produce replicas via normal polymer replication techniques, but should be inexpensive enough to be discarded when it fails or degrades. The secondary mould can

subsequently be used to transfer structures into another polymer, with a lower T_g . In [6] a polycarbonate-based polymer is used as the secondary mould material for replication in poly(methyl methacrylate) (PMMA) on opaque substrates. Similar polymeric moulds have been produced using mr-I 9000C-XP polymer on a 4-inch wafer [7].

Here, we describe a method for producing freestanding polymer replicas, for use in biomedical applications, using NIL. The high T_g polymer poly(ethylene naphthalate) (PEN) is used as the secondary mould, for the production of structures in PMMA. NIL is preferred over techniques such as hot embossing due to the high structural resolution, which opens the possibility of producing structures with nanometric dimensions. Hot embossing techniques tend to use parallel plate presses, which if misaligned by even a small degree reduces the lateral resolution of the imprinting process, typically to around 2 μm . In our case, the nanoimprint lithography apparatus is based on a hydraulic press which provides even pressure to the polymer/mould system and allows nanometric lateral resolution to be achieved [8]. We also describe the use of fluorinated ethylene propylene copolymer (FEP) as a support material when imprinting such structures.

2 Experimental

PMMA and PEN, both 125 μm thick, and FEP, 100 μm thick, were purchased from Goodfellow Ltd. (Cambridge, UK). Prior to use, the polymers were cut to the required size, thoroughly rinsed with propan-2-ol (Aldrich Chemical Co., USA), and dried under a stream of dry nitrogen gas. Moulds used for the imprinting of the polymers were designed in house and supplied by the Centro Nacional Microelectronica (CNM), Barcelona. The moulds consisted of silicon nitride (Si_3N_4) and/or oxide (SiO_2) coated

silicon. Into this surface coating the microstructures were defined using deep reactive ion etching techniques [9].

One of the problems with polymer imprint techniques is the possibility of the mould sticking to the polymer. The fabrication of the structures in the $\text{SiO}_2/\text{Si}_3\text{N}_4$ layers of the primary moulds was designed to combat this. The top surface of the mould structures was in each case Si_3N_4 which reduces the surface energy of the mould, compared to a silicon surface, and prevents polymer adhesion [10]. For a similar reason, the sidewalls of the structures were produced to be as vertical as possible. A monolayer fluoroalkylsilane anti-adhesion layer ((trichloro-tridecafluoro-octyl)silane, United Chemical Technologies, USA) was also added to both the primary and the polymeric secondary moulds to help eliminate any sticking problems. In the case of the primary mould, the monolayer was introduced to the mould surface in the liquid phase from a 10 mM solution of the silane in heptane, using a method described previously [10].

For the PEN secondary moulds, the silane was added via the vapour phase. The polymer was first rinsed thoroughly using acetone and dried under a stream of dry nitrogen. The mould was placed in a suitable glass container, within a desiccator, and a single drop of the silane placed in close proximity to the mould. The desiccator was evacuated, causing the silane to vaporise and coat the mould. The mould was left in the presence of the silane for 10 minutes before the vacuum was released and the mould removed. As the silane was not thought to physically adhere to the polymer surface, the polymer was rinsed with acetone and the silanisation was repeated before each subsequent imprint was performed. The PMMA replica was thoroughly rinsed with isopropanol to remove any traces of silane.

Polymer replication was achieved via imprint techniques using an Obducat nanoimprinter (Obducat AB, Sweden). The nanoimprinter operates using a pneumatic system in which the mould and polymer to be imprinted are placed on a stage and covered using a thin piece of aluminium. Application of a vacuum causes the aluminium to be compressed and form around the mould/polymer system. This holds the mould and polymer in place and stops any sliding of the mould when the pressure is applied. The imprint conditions depend on the polymer used for the replication (examples are given below). Characterisation of the surfaces of the moulds and the patterned polymers was achieved using optical microscopy and white light interferometry (Wyko NT110, Veeco Metrology, USA).

3. Results and Discussion

3.1 Fluorinated Ethylene Propylene Copolymer as a support layer

It is common in nanoimprinting to spin a thin film of the polymer for imprinting onto a substrate, such as silicon or glass. This substrate acts as a support for the polymer during the imprinting and ensures that any nanostructures are faithfully reproduced. Traditionally the structured polymer film is made as thin as possible to allow post-imprint operations to be achieved; for example, oxygen plasma removal of the residual polymer layer may be achieved with a view to metallising the substrate surface. For the production of sub-micrometer structured surfaces where transparency is advantageous (e.g. in applications such as fluidics) structuring of a freestanding polymer sheet would be preferable. We have recently shown this to be possible by sandwiching a freestanding piece of polymer between the mould and a second piece of the mould material [11].

Where the mould and its companion piece of supporting material is made of silicon, the uppermost piece of silicon has a tendency to fracture and break during imprinting (Fig. 1*a*). This causes pieces of silicon to become embedded in the polymer and the backside of the polymer to become patterned adjacent to the cracks in the silicon. Structures can be quite adequately imprinted in the polymer by removing the top piece of silicon and just having the aluminium sheet in contact with the back side of the polymer (Fig. 1*b*). However, this tends to cause the back side of the polymer to become imprinted with features present on the aluminium surface (due to the machining of the aluminium). This patterning of the back side of the PMMA reduces the transparency of the polymer film and consequently makes the final structure useless for transmittance microscopy applications. Replacing the silicon with a piece of FEP protects the back side of the PMMA from unwanted patterning by the aluminium while still allowing the polymer to be imprinted (Fig. 1*c*). The only drawback to this technique is that the back side of the PMMA is slightly wavy possibly suggesting an uneven applied pressure, although this does not affect the surface being imprinted. This could be rectified by using a thicker piece of FEP which should distribute the pressure more evenly.

UV/visible spectroscopy of the samples (Fig. 1*d*) shows that the PMMA structured using the PEN supporting material retains much of the transmittance of the non-structured PMMA. However, the samples structured using the other methods show a marked decrease in the amount of transmitted visible light. The reduction in the transmittance is due to scattering of the incident light by the increased surface roughness.

3.2 Poly(ethylene naphthalate) as a secondary mould

PMMA has been used as a polymer for the production of biomedical apparatus for some time now [2], whereas we have recently shown that PEN is a useful polymer for the production of such apparatus using polymer replication techniques [12]. Both of the polymers are biocompatible and can be used in imprinting techniques to produce freestanding films containing micro and nanostructures. Further, due to the optical transparency of the polymers in thin film form, they can be used to produce devices for applications where optical microscopy methods are required. Due to the significantly higher T_g of PEN, compared to PMMA, it is possible to use PEN as a secondary polymeric mould in NIL.

The first step in production consists of imprinting the PEN polymer replica using the silicon-based master mould. The PEN is typically imprinted using a silicon-based mould at 200 °C and 30 bar for 1200 s; the imprint time depending on the height of the structures to be imprinted. The PEN is sandwiched between the mould and a piece of FEP as previously described. The imprinting apparatus is closed and the entirety is heated to a temperature above that of the T_g of PEN before the embossing force is applied. After a predetermined embossing time, the temperature is reduced to below that of T_g and the pressure released. The mould/polymer system is then allowed to slowly cool to room temperature before the mould is carefully separated from the polymer. The silanisation of the mould ensures that the PEN can be easily separated from the silicon mould.

The second step of the replication technique is to use the silanised PEN as a mould in the production of superficial structures in PMMA. The PMMA is typically nanoimprinted at 130 °C and 30 bar pressure for 600 s. The PEN mould is placed on top of the PMMA, with the surface containing the superficial structures in contact with the

PMMA, and supported above and below both the polymers by FEP polymer. The imprinting proceeds as for the patterning of the PEN secondary mould.

A silicon-based mould with square post features $100\text{ }\mu\text{m}^2$ and $\sim 1\text{ }\mu\text{m}$ tall was used to produce the PEN secondary mould (Fig. 2a), producing a surface consisting of square holes of comparable dimensions (Fig. 2b). Subsequently, the PEN has been used to imprint square post structures in PMMA (Fig. 2c). Comparison of sectional profiles of the structures (Fig. 3) shows that they compliment one another. A slight rounding of the top surfaces of the PEN replica is seen, possibly due to incomplete filling of the silicon-based mould or due to shrinkage of the polymer via molecular relaxation upon cooling. Equating the structures in the mould and the replicas to truncated pyramids, the volume of the mould structure is $\sim 90\text{ }\mu\text{m}^3$. The volume of the cavity produced in the PEN is $\sim 71\text{ }\mu\text{m}^3$, suggesting that the PEN may suffer a 20% reduction in volume upon replication.

The rounding at the top of the PEN is then transferred to the bottom surface of the PMMA structures. This proves that the PMMA has fully replicated the structures in the PEN, however direct comparison of the structures (Fig. 3b) shows that the tops of the PMMA structures replicate those in the mould, but the valleys between structures are now less wide. The PMMA also shows some roughness on the top surfaces of its structures. This may be due to an insufficient covering of the anti-adhesion coating on the lower surface of the PEN mould and can be rectified by optimising the silanisation conditions used to coat the PEN surface. The height/depth of the structures in each surface are: silicon master mould $1.097\text{ }\mu\text{m}$, PEN secondary mould $1.109\text{ }\mu\text{m}$, and PMMA replica $1.105\text{ }\mu\text{m}$. Repeated PMMA replication of a 344 nm tall PEN mould (Fig. 4) gives an average height for 5 PMMA replicas of $339 (\pm 10)\text{ nm}$. The figure shows a

histogram of heights of the PEN mould and the PMMA polymer replicas: there are less points at the bottom of the PEN holes and at the top of the PMMA posts. In each case, the lower surface has been adjusted to zero. A few areas of the plots can be highlighted. At **A** the shoulder on the PEN peak is due to the rounded top edges of the PEN replica. Similarly, the small shoulders on the PMMA replicas at **B** are due to the rounded bottom edges of the PMMA which is replicated from the PEN. The negative values for the PMMA replicas at **C** are due to shrinkage in PMMA replica. This is evidenced by the lower surface of the PMMA, between the posts, being lower than majority of PMMA surface (as seen in fig 3b).

Finally, the secondary mould method was used to produce a PMMA sheet microstructured on both faces. The microstructured PMMA was produced by placing PEN moulds either side of the PMMA (Fig. 5). The PMMA replica in this case contains 5 μm diameter holes on one side and 10 μm diameter holes on the other.

4. Conclusion

We have presented an imprinting method using a high T_g polymer as a secondary mould for the production of structured, freestanding PMMA films. The freestanding replicas have the advantage that they can be used with standard microscopy techniques, while the use of a polymeric secondary mould preserves the valuable primary master. One of the possible applications for this technique is in the alignment of the mould with areas on the lower surface. If the polymer to be imprinted is spun onto an opaque substrate, and the mould itself is opaque, there can be problems when it comes to alignment of features. Using a transparent mould in this way allows the features to be

more simply aligned prior to imprinting. Alignment of moulds/polymers is a method that is currently under development for UV-based nanoimprinters using quartz moulds [13] with high precision alignment using techniques such as the Moire method [14]. Development of a cheap and durable polymeric mould to replace the quartz, and for use in conventional thermal nanoimprint apparatus, would be advantageous. In this case of course alignment optics must be available on the nanoimprint apparatus, which unfortunately was not available on the apparatus used here.

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Figure captions

- Figure 1 Optical images of PMMA imprinted using (a) a silicon backside support, (b) with no support and (c) with a PEF backside support. In each image, A is focussed on the micropatterned surface and B is focussed on the back side of the PMMA. The inset diagrams show the imprinting set up in each case, where 1 is the mould stamp, 2 is the freestanding sheet of PMMA and 4 is the covering aluminium layer. 3 is the silicon backside support in (a), and the PEF backside support in (c). (a) also shows an optical image of the fractured silicon on the PMMA. (d) shows the optical transmittance of each of the imprinted samples in the visible range, with unstructured PMMA (●), and PMMA structured using PEN (○), aluminium (▼), and silicon (▽) as the back-side support.
- Figure 2 White light interferometric images of (a) the primary Si₃N₄ mould, (b) the secondary PEN mould and (c) the PMMA replica, containing features with dimensions 10 μm², ~1 μm tall and 20 μm period. [Image area = 124 x 94 μm².]
- Figure 3 Sectional profiles of the data in Figure 2 are given; the data for the PEN has been inverted for comparison with the other data sets. In (a) the Si₃N₄ and PEN data has been offset on the y-axis for clarity, (b) gives the data overlaid for direct comparison.
- Figure 4 Normalised histogram of heights of 5 PMMA replicas of a 340 nm deep PEN mould. There are fewer points at the bottom of the PEN holes and at the top of the PMMA posts: the difference between the two peaks in each

plot corresponds to the height/depth of the structures. In each case, the lower surface has been adjusted to zero.

Figure 5 White light interferometric microscopy mages of PMMA embossed on both sides with (a) 5 μm diameter holes on one side, and (b) 10 μm diameter holes on the other [bars = 50 μm].

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5