euspen's 15th International Conference & Exhibition, Leuven, Belgium, June 2015
www.euspen.eu

Temperature dependent polymer shrinkage when replicating nanostructures

Morten Hannibal Madsen[1], Kai Dirscherl[1], Nikolaj A. Feidenhans'l[1,2], Poul-Erik Hansen[1], Jørgen Garnæs[1]

1: Danish Fundamental Metrologi A/S, Matematiktorvet 307, Kgs. Lyngby, Denmark.
2: DTU Nanotech, Technical University of Denmark, Kgs. Lyngby, Denmark.

Email: kdi@dfm.dk

Abstract
Polymers such as polydimethylsiloxane (PDMS) are widely used materials for replication of micro- and nanotextured surfaces and for fabrication of microfluidic devices. For metrological measurements using a replication technique one has to take the shrinkage into account. Here we report a study of the shrinkage of typical polymers for replication at the common used curing temperatures. The shrinkage factor, with its associated uncertainty, for PDMS in the range 40 °C to 120 °C is provided. By applying this correction factor, it is possible to replicate structures with an expanded standard uncertainty (k=2) of less than 0.4 % in lateral dimensions. It is also shown that fast curing polymers, such as the RepliSet-F5, have a negligible shrinkage at room temperature.

PDMS, Polydimethylsiloxane, shrinkage, replica, replication, microfluidic, RepliSet

1. Introduction

Replications of micro- and nanotextured surfaces are widely used in e.g. fabrication of microfluidic devices and for surface analysis [1]. Different types of polydimethylsiloxane (PDMS) are often used and have been demonstrated to replicate structures with lateral feature sizes down to 10 nm [2] and atomic step heights [3]. Commercial replication kits offer an easier and faster method but often lack replicating small feature sizes of typically <100 nm according to product specifications.

2. Replication technique

For the replication using PDMS, a mixture applying Sylgard 184 silicone elastomer kit (Dow Corning, USA) was prepared in a mixing ratio 1:10 of curing agent to base. The mixture was put under vacuum and stored for at least 30 minutes to remove trapped air bubbles. A sample was placed in a beaker and gently covered with the PDMS mixture as sketched in Fig. 1A. The beaker was then placed on a pre-heated hotplate until the PDMS was hardened. Typical hardening times were 2 hours, 4 hours, and 65 hours for curing temperatures of 21 °C, 60 °C, and 80 °C, respectively. The hardened PDMS was removed from the sample (Fig. 1B) and trimmed to fit under the microscope with a pair of scissors.
The commercial replication kits also consist of two compound mixtures. These are mixed directly before applying to the sample using special mixing nozzles as part of the kit. As the viscosity of these compounds is much lower than for the PDMS mixture, it can be applied directly on top of the sample without a beaker. A backing substrate is gently pressed on the backside of the applied compound. As the curing time is much shorter for the commercial kits, typically from one to 15 minutes at room temperature, no heating of the sample is necessary.

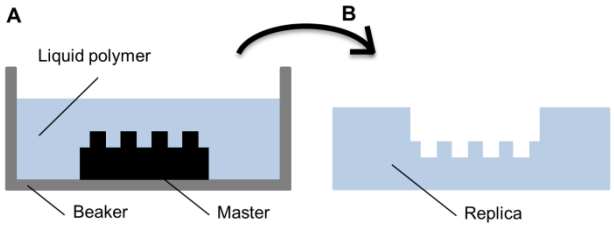

Figure 1. Sketch of the replication technique. (A) A liquid polymer such as PDMS is applied on top of a textured sample in a heat resistant beaker. (B) After hardening of the polymer it can be removed and one has a replica of the sample, that is, an inverted copy.

3. Measuring shrinkage

Transfer standards with a 2D checkerboard pattern were used as master structures for the replication. The transfer standards were etched in silicon and coated with a chromium and platinum layer to ensure an easy release of the polymers. The periods of the used transfer standards were measured in the x- and y-direction to (3001.1 ± 3.0) × (3001.9 ± 3.0) nm and (10.002 ± 0.010) × (10.008 ± 0.010) µm, where the values after ± indicate the expanded standard uncertainties given at the 95% confidence level (k = 2).

Measurements of the transfer standards and polymer replicas were acquired using a confocal microscope (Sensofar PLu neox) equipped with a 50x objective (NA = 0.80). A topographic image covering an area of 255 × 191 µm^2 was acquired for each sample in the center of the grid, with some typical examples shown in Fig. 2.

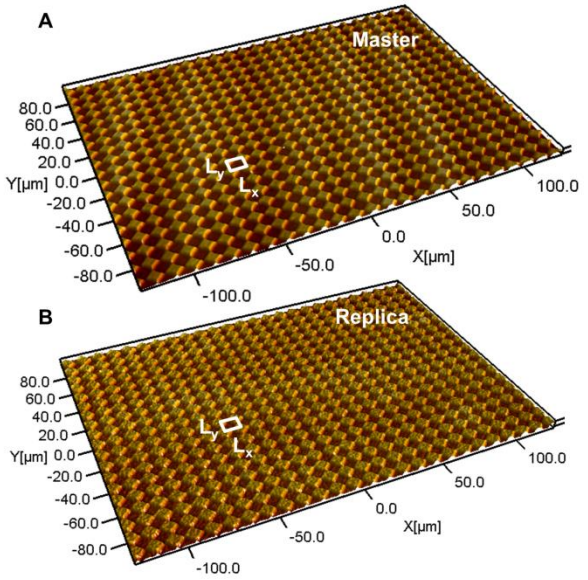

Figure 2. Topographic confocal imaging of a 2D checkerboard structure. (A) Transfer standard etched in silicon with a nominal pitch of 10 µm and a height of 100 nm. (B) Replica of the transfer standard using the fast curing polymer RepliSet-F5 at room temperature.

4. Experimental Data

It has been shown in Ref. [4] that one can account for the shrinkage of PDMS during hardening in the temperature range from 40 to 120 °C by applying a first order correction, $y = \alpha T + \beta$, where the fitting parameters are found to: $\alpha = 0.0180\ °C^{-1}$ and $\beta = 0.46$, with the expanded standard uncertainties $U(\alpha) = 0.0030\ °C^{-1}$ and $U(\beta) = 0.26$. After the correction, the expanded standard uncertainty on the lateral dimensions due to shrinkage is less than 0.4 % in the above stated temperature interval. All the ratios in this study are larger than the ones obtained by Lee and Lee [5]. This difference can be explained by a thinner PDMS layer in the study by Lee and Lee.

The shrinkage has been measured for fast curing polymers following the protocol from Ref. [4]. By measuring the master and replica with the same microscope conditions, relative measurements can be used to derive the shrinkage of the polymer. The dimensions of the unit cell for the checkerboard pattern, as indicated in Fig. 3A, is found by a 2D Fast Fourier Transform using the software package SPIP (Image Metrology), see Fig. 3B. For the polymer RepliSet-F5 (Struers) the shrinkage factor is found to (-0.07 ± 0.6) % for the replica at room temperature, where ± denotes the expanded standard uncertainty (k=2, equivalent to a confidence interval of approximately 95 %) of the measurement. The main contribution to the uncertainty is from the reproducibility of the replicas.

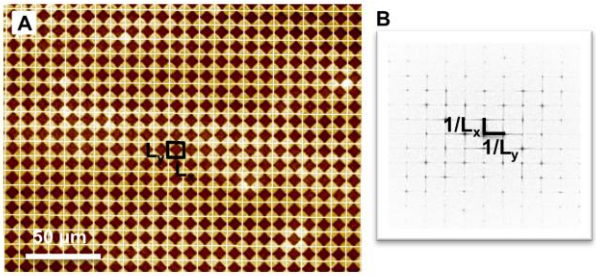

Figure 3. Image analysis. (A) Grid of unit cells overlayered the surface image of the RepliSet-F5 replica. (B) 2D Fast Fourier Transform of the image.

5. Summary

It has been shown that within the uncertainty of fabricating replicas of micro- and nanotextured surfaces the shrinkage of the polymer is negligible when curing at room temperature. For commercial replication kits, replicated structures can be analysed directly without having to apply corrections for the shrinkage. However, for pure PDMS based replication, curing at room temperature takes over 2 days and elevated temperatures are often used to reduce the curing time. A formula for correct the shrinkage of PDMS at temperatures in the range from 40 to 120 °C is provided.

Acknowledgement

The present research was supported by the Danish National Advanced Technology Foundation (NanoPlast) and Danish Ministry of Higher Education and Science (Documentation of micro-and nanotextured products, Industrial PhD Programme).

References

[1] Gates B D, Xu Q, Stewart M, Ryan D, Willson C G and Whitesides G M 2005 *Chem. Rev.* **105** 1171–96
[2] Gabai R, Ismach A and Joselevich E 2007 *Adv. Mater.* **19** 1325–30
[3] Elhadj S, Rioux R M, Dickey M D, DeYoreo J J and Whitesides G M 2010 *Nano Lett.* **10** 4140–5
[4] Madsen M H, Feidenhans'l N A, Hansen P E, Garnæs J and Dirscherl K 2014 *J. Micromech. Microeng.* **24** 127002
[5] Lee S W and Lee S S 2007 *Microsyst. Technol.* **14** 205–8