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# Patterning of Ultrasoft, Agglutinative Magnetorheological Elastomers

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**ABSTRACT:** A low-cost wax-cast molding technique for structuring ultrasoft (Young's modulus $\leq$ 40 kPa), agglutinative magnetorheological elastomer (MRE) material is presented. MRE structures ranging from a few millimeters down to the micrometer range with highly reproducible results are possible. Semitransparent MREs are also fabricated and their surfaces modified accordingly. This method opens new possibilities for MREs in biomedical engineering and microfluidic applications. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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## INTRODUCTION

Modification of surface topography according to a given impression (patterning) is a common task in the processing of polymers, in particular elastomeric materials.[1,2] Known methods of surface patterning work well for relatively hard polymers (Young's modulus $E > 10^2$ kPa) but fail when applied to softer materials, because these are usually agglutinative.[2,3] The major motivation for developing surface-patterning methods for soft, agglutinative elastomers results from soft-tissue engineering where the substrate materials for stem cell culture must be mechanically compliant with soft tissues.[3,4] In this respect, it appears that hitherto only one work,[3] addressing a similar problem has been published, where a sacrificial polyvinyl alcohol film as a transprinting media for microcontact printing on a soft, agglutinative polydimethylsiloxane (PDMS) substrate was used. The aim of the present work is to introduce a rapid prototyping process for the fabrication of either macropatterned or micropatterned ultrasoft ($E \leq 40$ kPa), agglutinative elastomers.

The proposed method is in general suitable for any soft, agglutinative elastomer. It will be demonstrated on the so-called magnetorheological PDMS-based elastomers (MREs),[5,6] where the choice is obviously determined by current scientific interests. Magnetorheological elastomer (MRE) comprises micrometer-sized ferromagnetic particles embedded into a PDMS matrix.[7–9] The very soft species may have Young's moduli $E_0$ down to $\sim$ 10 kPa. $E_0$ denotes the Young's modulus in the absence of a magnetic field. By applying an external magnetic field, this Young's modulus can be increased by up to more than two orders of magnitude. In addition, reversible inhomogeneous deformation and surface movements can also be induced by magnetic field variations. Considering the balance of magnetic and elastic contributions to the energy density, it has been shown[10] that the strain $\varepsilon$ due to the externally applied homogeneous magnetic field (the so-called magnetostrictive effect) is in the first approximation inversely proportional to the square root of the shear modulus $G_0 \approx E_0/3$ of the MRE in the absence of a magnetic field: $\varepsilon \sim G_0^{-1/2}$. Hence the deformation is enhanced in softer MREs. This opens up possibilities for several new applications, for example, in the field of electromechanical devices (actuators). In recent years, there has been growing interest in the development of actuators using MREs and their respective miniaturization.[10,11] Surface patterning of MREs is an obvious way to provide functionality, for example, for miniature actuators. In soft-tissue engineering, soft MREs can be used as mechanically compliant cell substrates with magnetically tunable rigidity. Depending on the application field (actuators or tissue engineering), either macropatterns ($\sim$ 1–10 mm) or micropatterns ($\sim$ 1–10 $\mu$m) are required.

The usual methods of MRE production and forming are injection molding,[12–14] compression molding,[13,14] cast molding,[14,15] and vacuum-assisted resin transfer molding.[15] To form a topographically defined periodic PDMS surface, a template-free wrinkle/crack formation can be used.[3,15]

Currently, polytetrafluoroethylene (PTFE, Teflon®) molds are used for agglutinative elastomers, in particular soft MRE. Because of its exceptional antistick properties,[16,17] the MRE can be removed more easily. In general, PTFE is not easy to handle, because its melting point is higher than the decomposition temperature. This property prevents processing using low-cost thermoplastic procedures.[2,18] Further disadvantages of using PTFE molds are the strong volume change at room temperature and surface porosity.[18,19] Recently,[20] the MREs were structured by molding a methylmethacrylate board that was then laser-etched. This is a rather sophisticated and expensive procedure. The search for alternative low-cost molding materials is justified. As shown below, the mold material of choice is wax, because it is easy to work with, is reusable, and has a similar low surface tension to PTFE. Patterned wax is currently used in miniaturized systems such as lab-on-a-chip in microfluidic applications[21–24] or in decal transfer microlithography.[25]

In the field of semiconductor fabrication, many methods for micropatterning are well established. Consequently, a structuring method has been selected, which has similar sequences to the well-known soft lithography.[26–29] This patterning method is based on a newly developed technique, which will be referred to as "wax-cast-molding" in this work.

The work is organized as follows: first, the materials used and their preparation are described. The methodology of wax-cast-molding for both macroscopic and microscopic structures is presented in the following section, where the examples of application of this method for patterning ultrasoft MREs are also given. The results are summarized in the concluding section.

## EXPERIMENTAL

### Magnetorheological Elastomers

**Material.** A vinyl-terminated PDMS served as base polymer. In addition, various additives such as hydride functional silane and a solvent-based platinum catalyst were used. The components of these crosslinkable polymers are commercially available from several suppliers. Pure carbonyl iron powder (CIP), provided by BASF (mean particle size of 4.5 $\mu$m, type SQ), was used as ferromagnetic filling material.

**MRE Preparation.** MRE samples are prepared by crosslinking of a liquid silicone rubber dispersion containing 30% of CIP by volume to maximize the changes in the mechanical properties by the magnetic field.[30,31] The cross-linking is accomplished by means of Pt-catalyzed polyaddition of vinyl-terminated PDMS and a polymeric hydrosilane as a cross-linking agent. To establish an ultrasoft MRE, a loosely cross-linked polymeric network is required. For this purpose, a base silicone rubber formulation containing dispersed CIP in vinyl-terminated PDMS was developed. For the curing, that is, vulcanization process of this base formulation, a polymeric cross-linking agent with only a few cross-linking sites was found to be the most suitable. Following hand mixing of the monomer and powder, outgassing under vacuum for 10 min, curing was completed within 24 h at room temperature.

### PDMS Used for Transparent Base

**Material.** The manufacture of polydimethylsiloxane (PDMS) networks is carried out by the cross-linking of two components. Sylgard® 184 is a commercially available silicone elastomer from Dow Corning S.A. It has been prepared from a linear PDMS prepolymer (Sylgard® 184 A), which possesses vinyl end groups. This first component can be linked using a platinum hydrosilation with methylhydrosilan (Sylgard® 184 B).

**PDMS Preparation.** These two components Sylgard 184 A and Sylgard 184 B are mixed in a ratio of 10 : 1 by weight, as described in the product information.[32] Following air bubble removal by vacuum evacuation for about 15 min in an exsiccator, cross-linking can be performed at room temperature.

### Waxes

Wax-containing aqueous release agents are often used to separate silicones from other materials. In this case, waxes in fixed form, meeting the following requirements, are needed:

- accurate reproduction
- low-thermal contraction when cooled
- ease of handling
- good modeling properties
- shape stability

To identify a wax ideally suited to this application, various commercially available types were investigated.

In Table I, a selection of waxes and some of their properties such as elastic indentation modulus ($E_{IT}$)[*] and Martens hardness (HM)[33] together with their relevant advantages and disadvantages are listed. For the determination of mechanical properties, the microhardness meter Fischerscope HM2000 from Helmut Fischer GmbH, Germany, was used.

After producing the first wax replicas, it became apparent that carnauba wax is very well suited for micropatterning. In comparison with other waxes, it is hard (see Table I) and dimensionally stable, and therefore the same material can be used as a form-master several times. For the macrostructuring, this wax is not so appropriate, because it tends to break during cooling. As a result, modeling wax (Weiton-modeling wax[34] from Johannes Weithas KG, Lütjenburg, Germany), which finds its use in the dental sector, was chosen for macromodeling. This wax can be molded very easily and remains elastic, enabling ease of MRE removal on completion.

### Silicon-Master

**Material.** As a basis for the required microstructured masters, double-sided polished *n*-type (phosphorus doped, $\rho \sim$ 1–8 $\Omega$cm) silicon wafers with (100) orientation were used.

**Silicon-Master Preparation.** Following a dehydration bake, a negative photoresist (AZ5412 from AZ Electronic Materials) was spinned onto the silicon wafer before undergoing a soft-bake process. To dry the photoresist, the coated wafer was then mounted on a hotplate at a temperature of 105°C for 1 min. With the help of a mask aligner, the structures of a patterned chrome photomask were transferred onto the coated surface of

[*]Elastic indentation modulus can be considered as an estimate of a Young's modulus ($E_{IT} \approx E$).

**Table I.** Different Wax Types: Comparison of Their Mechanical Properties

| Wax type | $E_{IT}$ (MPa) | HM (N mm$^{-2}$) | Pro | Con |
|---|---|---|---|---|
| Bees wax | 737.5 | 34.6 | Elastic easy handling | Adhesive fragile |
| Carnauba wax (bright) | 1488.9 | 49.7 | Good modeling | Fragile |
| | | | Shape stability | |
| | | | Accurate reproduction | |
| Carnauba wax (dark) | 1755.9 | 67.4 | Good modeling | Fragile |
| | | | Shape stability | |
| | | | Accurate reproduction | |
| Paraffin wax | 501 | 23.4 | Easy handling | Crystalline fragile |
| Modeling wax | 93.6 | 1.2 | Elastic | Adhesive |
| | | | Easy handling | |
| | | | Good modeling | |
| | | | Shape stability | |
| | | | Low-thermal contraction | |

the wafer using a contact method using ultraviolet light with energy density of 90–100 mJ/cm$^2$. Following exposure, the photoresist was developed by the addition of an AZ-developer (AZ Electronic Materials). The photolithography was then followed by a dry-etching step using reactive ion etching based on $SF_6$ gas with an etch rate of 450 nm/min. This process was carried out on an Oxford Plasmalab80 (Oxford Instruments) reactor. Afterward, the remaining photoresist was removed with acetone. Figure 1 shows a raster electron microscope image of a typical silicon master.

## RESULTS AND DISCUSSION

The production of a patterned MRE involves two main steps: the preparation of the wax mold and the actual fabrication of the structured elastomer. These manufacturing steps are different depending on the required structure dimensions. Therefore, the structuring methods are divided into two groups: macropatterning and micropatterning.

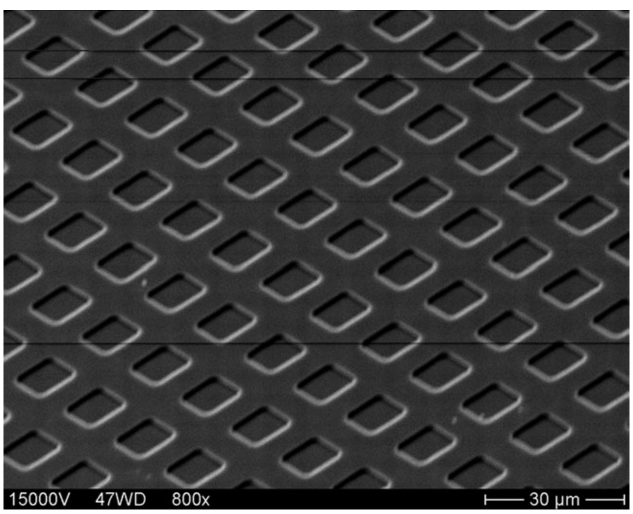


**Figure 1.** Raster electron microscope image of an etched silicon-master with square pits.

### Macropatterning

As shown in Figure 2, there are several process steps necessary to complete a structured MRE. Production of the macroscopic wax-cast molding and the manufacture of patterned MRE will

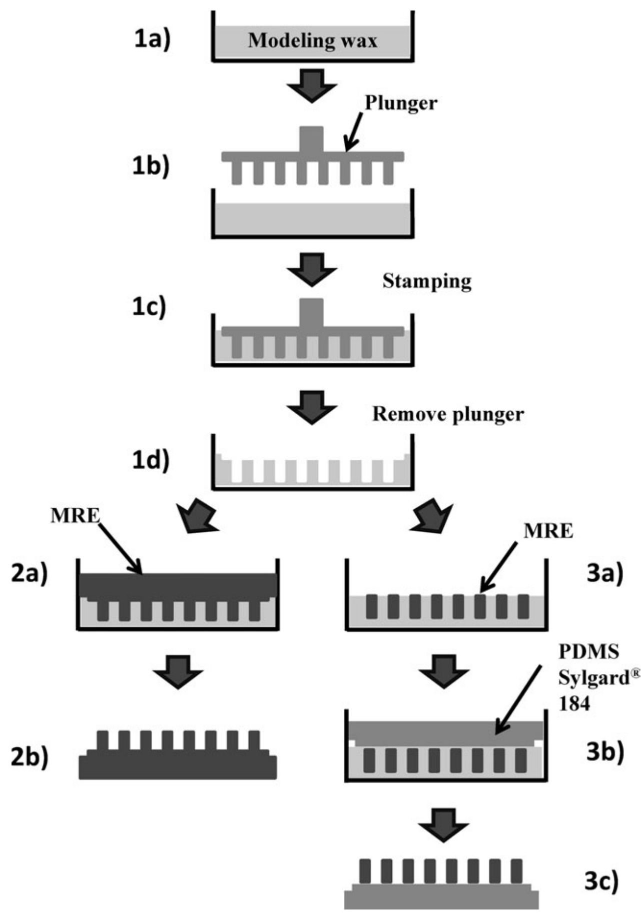


**Figure 2.** Schematic diagram of the mold fabrication process for macroscopic wax-cast-molding and resulting patterned MRE. Steps 2a and 2b refer to a nontransparent MRE. Steps 3a–3c show fabrication of a semitransparent structure.

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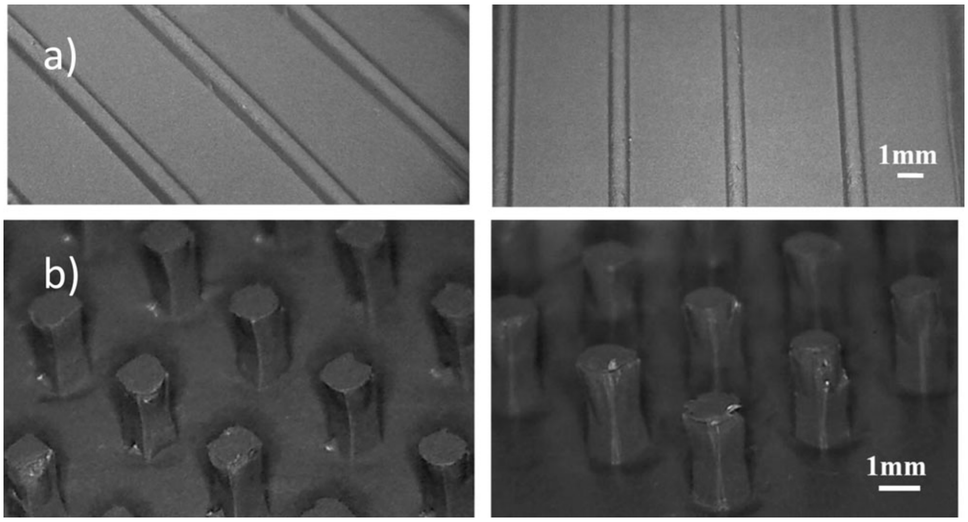


**Figure 3.** Macroscopic MRE structures from various perspectives: (a) longitudinal MRE-lines and (b) quadratic MRE columns.

be described step by step. The manufacturing of structured MRE can be separated into two main sections:

- production process of the mold for the macroscopic wax-cast-molding (Figure 2; steps 1a–1d)]
- fabrication of the patterned MRE (Figure 2; steps 2a and 2b)

As shown in Figure 2(1a), for the macromodeling, the Weiton dental modeling wax is fitted into a container where it can be easily molded and remains elastic, facilitating MRE removal later. This wax is structured with the help of an embossing tool, which is manually pressed into the modeling wax [see Figure 2(1b,1c)]. After removal of the tool, a structured wax master remains in the container as shown in Figure 2(1d).

On completion of the wax master, fabrication of the patterned MRE follows. After the monomer was mixed with the powder by hand and outgassing under vacuum for 10 min, the mixture was inserted into the wax master as shown in Figure 2(2a). Because the modeling wax melts at relatively low temperature (melting point: 56–58°C[34]), curing was easily completed within 24 h at room temperature.

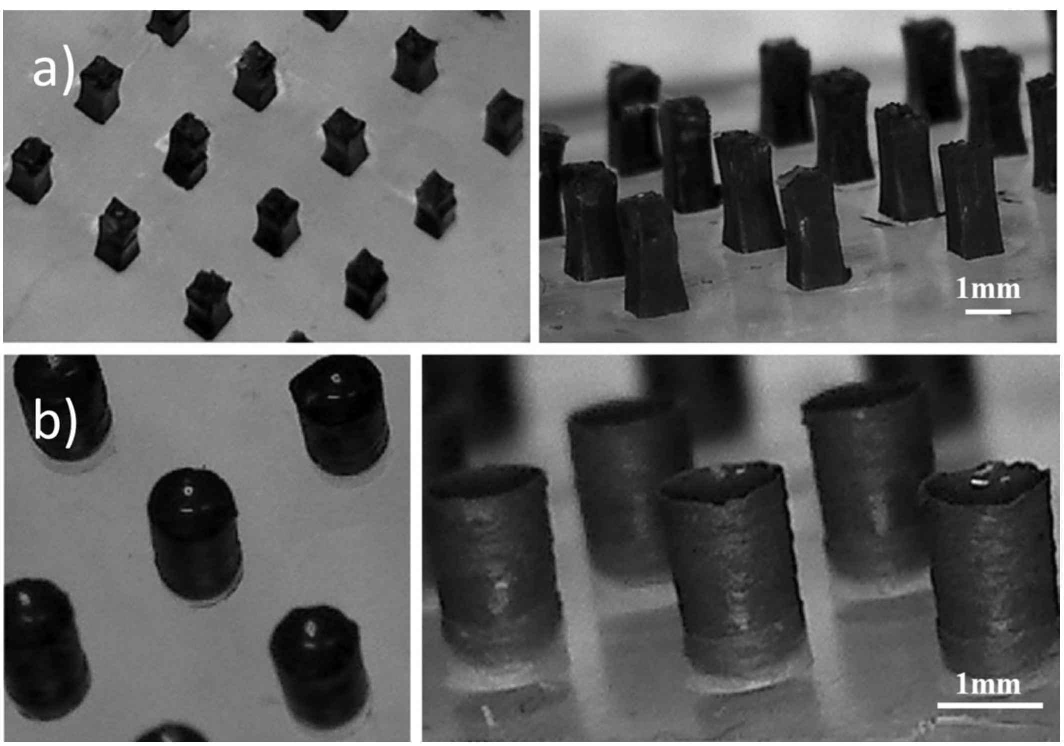


**Figure 4.** MRE columns on a transparent substrate from various perspectives. (a) Quadratic and (b) cylindrical.

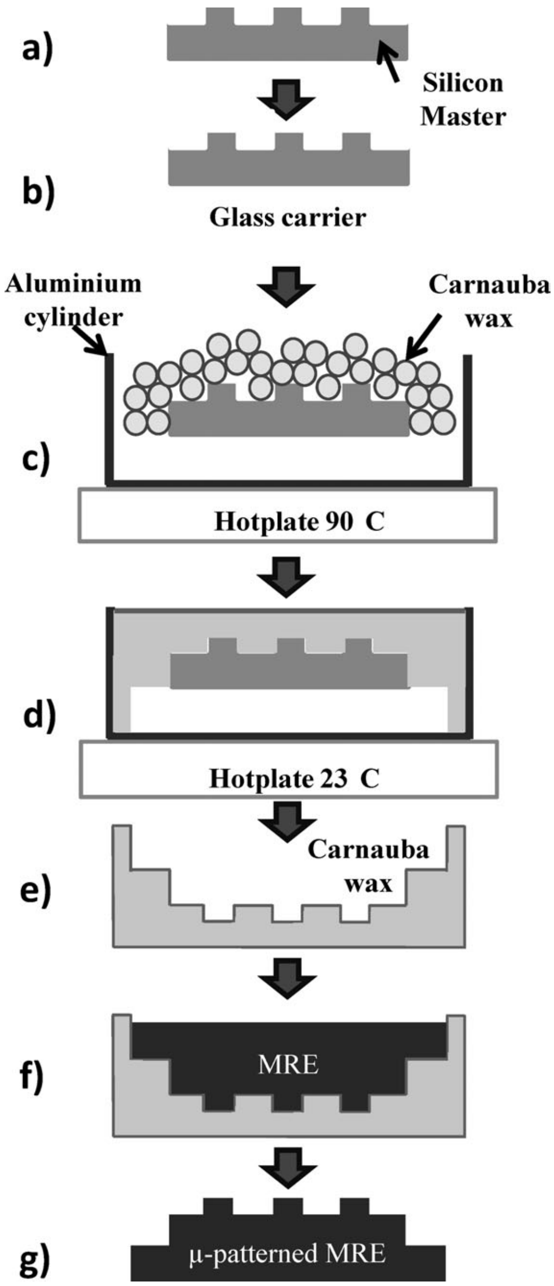


**Figure 5.** Schematic diagram of the fabrication process of the mold for the microscaled wax-cast-molding and the resulting patterned MRE. MRE denotes the elastomer.

As shown in Figure (3a), it is possible to produce lines of 1 mm width over the whole MRE surface. It can be observed that the surface has been molded smoothly and without large deviations. Figure 3(b) shows well-made MRE columns with a width of 1 mm and a height of 2.5 mm.

### Semitransparent Structures

In addition to simple-patterned MRE, it is also possible to produce semitransparent MRE. As shown in Figure 2, the same wax master has been used and also prepared in the same way as described earlier. However, the fabrication of semitransparent MRE itself is somewhat different.

Figure 2 (step 3a) shows that the liquid MRE mixture has been injected into the holes of the wax master, after which unfilled PDMS (Sylgard 184) was applied onto the MRE [see Figure 2 (step 3b)]. The Sylgard 184 was prepared from two components Sylgard 184 A and Sylgard 184 B, which were mixed in a ratio of 10 : 1 by weight as described in the product information.[32] Air bubbles were evacuated from the fluid Sylgard in an exsiccator for about 15 min. Curing of the MRE and Sylgard 184 was completed within 24 h at room temperature. Because the MRE is soft ($E_{it} \approx 40$ kPa), the hard Sylgard substrate ($E_{it} \approx 2.5$ MPa) helps to stabilize the structure.

Figure 4 shows examples of semitransparent MREs. It is possible to produce both quadratic and round columns using this method. As can be seen clearly, these columns are mounted on a transparent layer.

### Micropatterning

Here, a simple replication technique for micropatterned MREs is presented. The silicon master fabrication is based on standard semiconductor manufacturing processes as described earlier. Figure 5 shows the schematic diagram of the production process of the mold for the microscaled wax-cast-molding and the resulting patterned MRE.

As shown in Figure 5, step b) by the silicon-master has been bonded to a glass carrier. If the master had not been placed on it, it would be more difficult to remove it from the wax afterward. This molding tool was placed in an aluminum cylinder, preheated to 90°C, after which it was covered with wax [see Figure 5 (step c)]. Carnauba wax melts at 80°C and is particularly well suited for micropatterning as it is relatively hard (Table I) and dimensionally stable allowing it to be reused as a form master. Figure 5 (step d) shows the wax melted over the molding tool. Cooling was performed at room temperature. After cooling and removal of the silicon master, a molding tool made from carnauba wax has been achieved [see Figure 5 (step e)].

As described earlier, the MRE samples were prepared by mixing liquid silicone rubber dispersion containing 30% of CIP by volume. After exsiccation under vacuum for 10 min, the mixture was put into the wax master, as shown in Figure 5 (step f), before a further exsiccation process removed all remaining air bubbles. Curing was completed within 24 h at room temperature.

Figures 6 and 7 show some examples for microstructured samples. As shown in Figure 6, it is possible to produce microscaled 10 $\mu$m × 10-$\mu$m quadratic pits. It is obvious that silicon master, wax, and MRE were micropatterned. Figure 7 demonstrates that large areas can also be microstructured using this method; here, a total area of 7 mm × 7 mm with pins of ~ 6 $\mu$m diameter was processed.

The proposed method is applicable to any soft, agglutinative elastomer. It must not possess magnetorheological properties in order to be structured. In comparison with conventional MREs, those used in this work are distinguished by their low-Young's moduli < 40 kPa. Typical MR shear moduli $G'$ as a function of

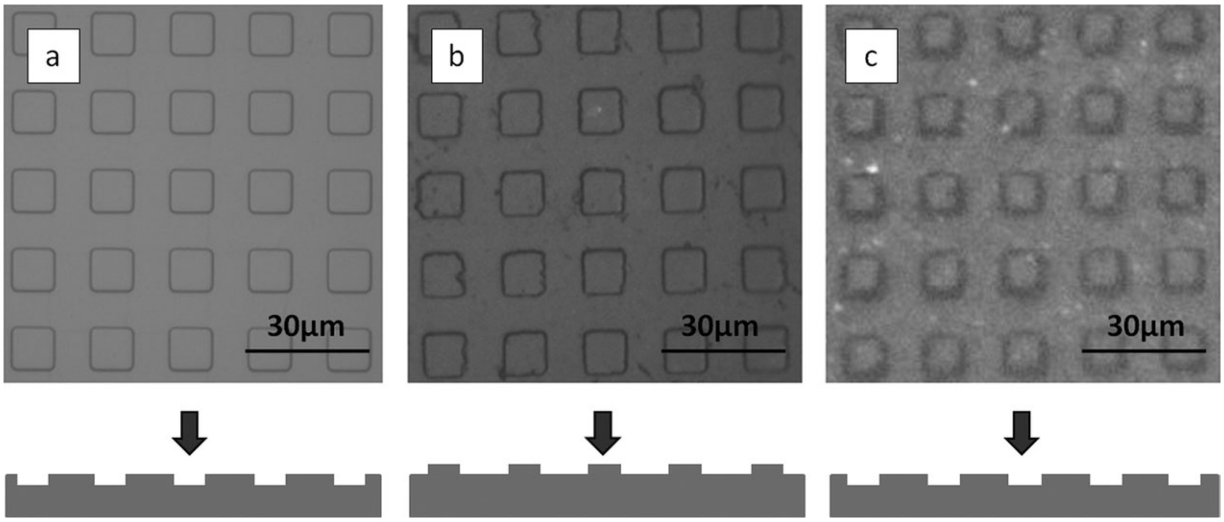


**Figure 6.** Optical microscope images of microscaled quadratic pits: (a) silicon master; (b) carnauba wax master; (c) patterned MRE. The last row illustrates the profile of the corresponding material.

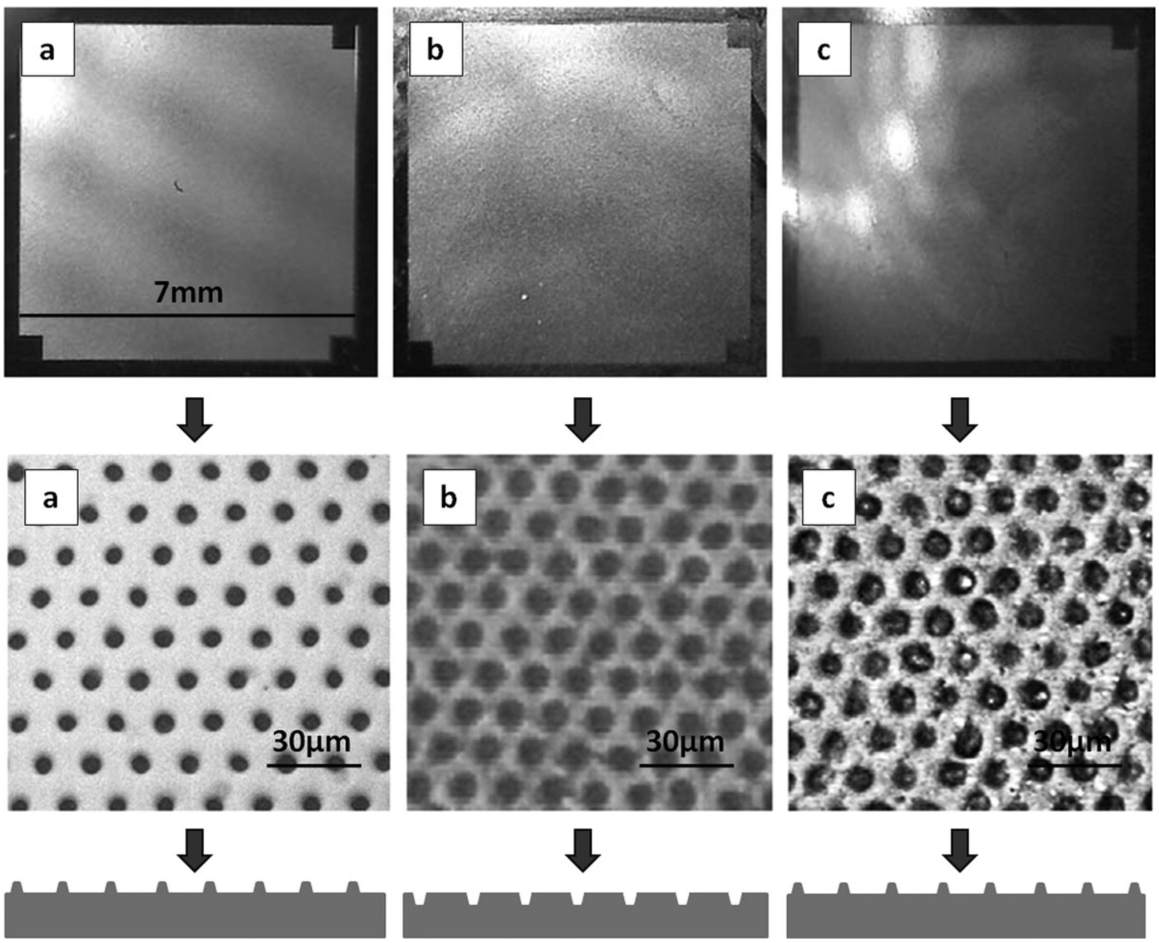


**Figure 7.** Results of the fabrication process for the MRE surface structured with microscaled pins. Upper row: General view of the silicon master (a), the carnauba wax master (b), and the patterned MRE (c). Middle row: Optical microscope images of the silicon master (a), the carnauba wax master (b), and the patterned MRE (c). The lower row illustrates the cross-section of the corresponding material.

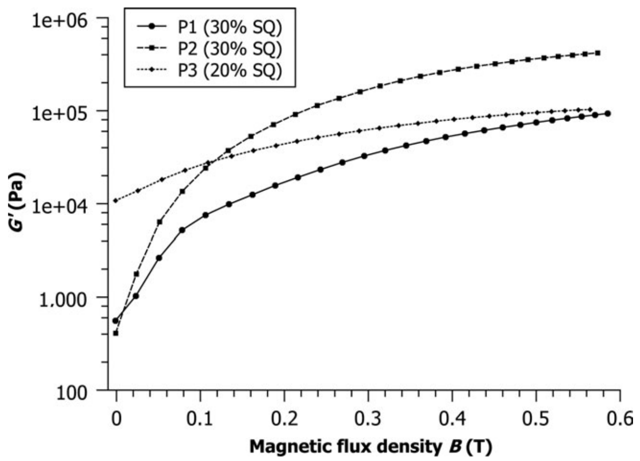


**Figure 8.** Shear modulus $G'$ of typical used MRE samples as a function of the magnetic flux density $B$ as measured using an Anton Paar rheometer with a modified magnetorheological device (MRD-MD170, PP20). The oscillating measurement conditions are constant angular velocity $\omega$ of 10 $s^{-1}$, constant shear deformation of 0.1%, and a constant temperature of 20°C. The sample geometry is 20-mm diameter and 3.5-mm thick.

an externally applied magnetics flux density $B$ (as measured on Anton Paar MCR 301 rheometer) are shown in Figure 8.

Hitherto, magnetorheological effects of bulk MREs have mainly been used for shock and vibration absorbers, as described in a number of previous publications. Applications using surface-structured MREs have not been so intensively investigated. In future work, it is intended to investigate the combined influence of surface topography and the magnetically tunable Young's modulus of PDMS-based MRE cell substrates on living cells for biomedical applications. Other prospective applications are the lab-on-a-chip devices to be magnetically controlled using flow barriers or pumping systems.

## CONCLUSION

In this work, a low-cost wax-based molding technique for the surface structuring of ultrasoft ($E \leq 40$ kPa) and agglutinative MREs has been presented.

The necessary procedures for both macropatterning and micropatterning of MRE structures from a few millimeters down to some micrometers have been described in detail.

In addition to several types of macro and microstructured elastomer, semitransparent MREs have also been produced and their surfaces modified accordingly.

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