Microfabrication of 3D Structures Using Novel Thermoplastic Elastomers

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ABSTRACT

The use of thermoplastic elastomer gels as advanced substrates for construction of complex microfluidic systems is shown. These gels are synthesized by combining inexpensive polystyrene – (polyethylene / polybutylene) – polystyrene triblock copolymers with a hydrocarbon oil for which the ethylene/butylene midblocks are selectively miscible. The insoluble styrene endblocks phase separate into localized domains to form an optically transparent, viscoelastic, and biocompatible 3-D network (similar to PDMS), with the further advantage of melt-processability in the vicinity of 100 °C. Microfluidic devices can be fabricated in under 5 minutes by making an impression of the negative relief structures on a heated master mold. Multiple impressions can be made against different masters to construct geometries incorporating variable-height features, as well as intricate 3-D multilayered structures. Thermal and mechanical properties are tunable over a wide range through proper selection of gel composition.

Keywords: microfluidics, PDMS, thermoplastic elastomer, rapid prototyping, soft lithography

1 INTRODUCTION

The development of increasingly sophisticated chemical and biochemical assays, combined with the need to incorporate these processes within a compact device footprint suitable for massively parallel operation requires the construction of correspondingly complex microfluidic structures [1,2]. This ongoing drive toward increased device complexity requires corresponding advances in fabrication materials and technologies. For example, although a number of multilayer PDMS-based systems have been successfully constructed, the resulting fluidic networks are effectively 2-dimensional owing to the planar nature of the fabrication process. It is possible in principle to employ an arbitrary number of layers, however the entire device structure must be assembled at once due to the irreversibility associated with the curing process. This irreversibility can be advantageous in terms of ensuring excellent mechanical stability, however it also imposes limitations because the molded structures cannot be further modified after curing. Consequently, there is no straightforward process to fabricate structures incorporating features of variable height because only a single impression from a single master can be used. Finally, the range of viscoelastic properties available for design of fluidic components that operate by inducing deformations in the substrate material (e.g. valves, pumps) is somewhat limited.

2 THEORY

Novel thermoplastic elastomer gel substrates offer the capability to provide a greatly enhanced level of flexibility in microfluidic device design and construction. These gels are easily synthesized using a combination of inexpensive polystyrene – (polyethylene / polybutylene) – polystyrene (SEBS) triblock copolymers in hydrocarbon oils for which the ethylene/butylene midblocks are selectively miscible. The thermodynamic incompatibility between blocks induces microphase separation and self assembly of the insoluble polystyrene endblocks into distinct domains with characteristic size scales on the order of 10-20 nm [3,4]. The soluble midblocks emanating from these nanodomains penetrate into the solvent creating arrays of loops (beginning and terminating within a single nanodomain) and bridges (joining adjacent nanodomains) resulting in the formation of a 3-D viscoelastic gel network in which the polystyrene domains act as physical crosslink junctions. Like PDMS, this gel network is optically transparent, viscoelastic, and biocompatible, but also possesses the further advantage of melt-processability at temperatures in the vicinity of 100 °C.

3 EXPERIMENTAL

A series of thermoplastic elastomer gels were synthesized by combining commercially available SEBS copolymer resin (e.g. CP-9000, Kraton-G series) in mineral oil. The resin and mineral oil were mixed and placed under vacuum overnight at room temperature in order to allow the oil to evenly wet the resin surface. The mixture was then heated to 120-170 °C (higher temperatures are required with increasing copolymer fraction) under vacuum for 2–4 hours to allow the resin and oil to intermix and to remove any residual air bubbles. Finally, the mixture was cooled to room temperature and the solidified gel was cut into smaller pieces used for molding devices. Gel compositions ranging from 9 to 41 wt% copolymer were studied.

4 RESULTS AND DISCUSSION

We investigated thermal transitions associated with these SEBS-mineral oil gels using small amplitude oscillatory shear experiments (Fig 1). A measure of the transition to liquid-like behavior can be inferred from the
temperature $T^*$ at which the value of the loss modulus $G''$ exceeds that of the storage modulus $G'$. The range of gel compositions studied here allow the location of this transition to be varied over a range of approximately 50 °C. Moreover, the room temperature (plateau) value of the elastic modulus can be varied over an order of magnitude.

Individual layers are repositionable, thereby allowing precise alignment to be achieved prior to thermal bonding. More complex 3-D structures can be fabricated by direct casting (Fig 3), and interfaces with external fluidic supply lines can be readily sealed by locally heating the gel to melt it at the point where the lines are inserted into the substrate. An alternative fabrication approach involves directly embedding an intertwined bundle of fluidic channels within a bulk elastomer slab by dipping the channels into molten elastomer. Upon cooling, the channels become seamlessly embedded in the bulk gel, allowing the fabrication of braided or knotted flow geometries (Fig 4). Choosing a lower wt% gel formulation for the bulk material ensures the channels will remain intact during the embedding process.

![Figure 1: Variation of melt transition temperature (top) and plateau elastic modulus (bottom) with gel composition.](image)

Fabrication of microfluidic devices is accomplished by placing a slab of elastomer on top of a master mold that has been preheated to 120 °C on a hot plate. Within seconds the elastomer begins to soften, after which a glass plate is placed on top of the slab and gentle pressure is applied by hand to ensure complete contact with the structures on the mold. After cooling and release, the solidified gel incorporates the shape of the structures on the master (Fig 2). Strong uniform bonds can be easily achieved, either with a glass or elastomer surfaces, by briefly heating the material to a temperature just below its softening point either on a hot plate or using a handheld heat gun. The entire fabrication process can be completed in about 5 minutes. We are also able to easily assemble a variety of complex multilayered structures in only a few minutes (Fig 2).

![Figure 2: Planar (left) and interconnected multilayer (right) microfluidic channels constructed using elastomer gels (400 x 30 μm cross-section).](image)

Perhaps the most compelling advantage of elastomer gel substrates is that, unlike PDMS, multiple impressions can be made against different masters to easily construct complex geometries incorporating variable-height features within the same channel network. After an initial impression is made using the first master, any number of subsequent impressions can be made in the same elastomer slab using different masters containing features with distinct heights and/or shapes (Fig 5).
We have demonstrated the suitability of these elastomers as substrates for microfluidic applications by constructing devices for DNA electrophoresis and diffusive transport studies [5]. We further investigated biocompatibility of these elastomer materials by performing a $Eco$ RI restriction digestion reaction on a lambda phage DNA target. Parallel reactions were performed using both untreated 0.2 mL reaction tubes, and tubes whose inner surfaces were coated with 23 wt% elastomer gel. All five digested bands were visible after 1 hour of incubation at 37 °C in both the untreated and elastomer coated tubes, thereby demonstrating a high level of compatibility with standard biochemical reagents and protocols (Fig 6).

The high degree of versatility and fabrication ease, combined with their inherently inexpensive nature, make thermoplastic elastomer gels ideal substrates for many microfluidic applications.

**REFERENCES**