SELF-ROLLED POLY(DIMETHYL SILICONE) MICROCAPILLARIES WITH ENGINEERED INNER SURFACE: NEW FUNCTIONAL ELEMENTS OF MICROFLUIDIC DEVICES

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ABSTRACT

We propose a microfluidics device whose main functional part consists of a microcapillary produced by the self-rolling of a thin poly(dimethylsiloxane) film. Rolling is caused by inhomogeneous swelling of the film, pre-treated by oxygen plasma, in the vapour of chloroform. The capillaries are integrated with external electrical circuits by co-rolling electrodes and micro-resistors. The local control of temperature in the tubes by Joule heating is illustrated via the rate of an intra-tubular chemiluminescent reaction. The novel tubes with engineered inner structure can find numerous advanced applications such as functional elements of integrated microfluidics circuits.

KEYWORDS: Poly(dimethyl siloxane), Inner Surface, Self-rolling, Microcapillary

INTRODUCTION

Topography and physico-chemical properties of the inner walls of microcapillaries play an important role in the processes investigated in capillary chromatography, microfluidics, and the flow and phase transitions of complex fluids in confined media. Recently, a novel approach to the fabrication of microcapillaries was introduced, which provides unprecedented opportunities for the engineering of their interior. The approach is based on the micromechanical phenomenon of self-rolling of thin films of different nature (metals and oxides [1], semiconductors [2-5], polymers [6-8]) due to the internal stresses in the films. When the stress is inhomogeneous in the direction normal to the film, a bending moment arises, which leads to film detachment from the substrate, and to rolling. A number of research groups have worked on self-rolled tubes and scrolls for applications as different as micro-syringes for single-cell operations [2], X-ray waveguiding [3], micro-fluidics [4], living cell and drug encapsulation and release [6], and optical resonators [5]. The interior of the micro-capillaries has been engineered through the use of a number of surface modification techniques, such as plasma treatment, metallization, photolithography, etc [8]. The application of conventional two-dimensional lithography scrollable semiconductor films enabled integration of high-performance field-effect transistors [9] and GMR sensors [10] into the rolled-up microfluidic channels. The progress in this field has recently led to the introduction of the “Lab-in-a-tube” concept [11].

In the present work [12] we introduce micro-scale capillaries formed by the self-rolling of poly(dimethylsiloxane) (PDMS) thin films, and demonstrate the integration of these capillaries with fluids and electrical circuits. PDMS is broadly used in microfluidic systems due to a number of remarkable properties such as optical clarity, thermal stability, biocompatibility, and chemical inertness. Therefore, the rolled-up microcapillaries based on this material inherit these properties and are well suited to the traditional application objectives of microfluidics research. To demonstrate the possibilities provided by the approach, we consider the control of the rate of a chemiluminescent reaction inside a PDMS capillary via Joule heating with the use of an encased electrical circuit.

EXPERIMENTAL

A thin film of poly(4-vinyl pyridine), (P4VP, 60 kDalton, Sigma Aldrich) was formed on a glass slide by spin-coating from solution in chloroform. Glass slides were used as is, without additional cleaning. PDMS (Sylgard 184) with a standard base to curing agent ratio of 10:1 was spin-coated or dip-coated over the P4VP film. The spin-coating rate was varied between 3000 and 5000 rpm, and the time of the procedure changed from 15 to 120 seconds. For dip-coating, toluene was added to PDMS in a proportion of 1:1, in order to reduce the viscosity of the fluid, and the rate of lifting of the substrate from the solution was set to 1 mm/s. The PDMS film was thermally cured in an oven at 80°C, for 1 hour. The samples were then treated by oxygen radiofrequency plasma (Plassys MDS 130, at a pressure of 2x10^-1 mBar, or Diener Femto O₂, at 30 mBar), and a power of 100 W, for time intervals varying from 1 to 30 minutes. The PDMS layer was structured with a Trumark 6330 marking laser system, a pulsed d:YVO4 laser which operates at a wavelength of 355 nm. A laser beam with a pulse frequency of 20 kHz at 100% power, and a spot diameter of 30 μm, was guided over the sample at a speed of 30 mm/s. The structured films were placed in a closed vessel containing chloroform vapour, avoiding contact of the films with the solvent liquid phase. The rolling of the tubes was observed after a few minutes and could be stopped at any instant by taking the system from the vessel.

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RESULTS AND DISCUSSION
The fabrication scheme. The fabrication of the tubes (figure 1a) starts by covering a glass slide by a thin film of poly(4-vinyl pyridine) either by spin or dip coating. The role of this layer consists in reducing the adhesion of the PDMS films to the substrate during the tube rolling in chloroform vapour. PDMS is deposited on the substrate by spin coating or dip coating. PDMS films with thicknesses between 10 and 36 $\mu$m were obtained through variation of the spin or dip-coating rates, and the fraction of toluene added to the mixture of PDMS with the curing agent. After curing the films, the samples were exposed to a radiofrequency oxygen plasma which created an oxidized layer on the surface of the polymer composed of a mixture of the original polymer and silicon bonded to three or four oxygen atoms (SiO$_x$) [13]. This relatively rigid ceramic film creates a counterforce to expansion of the bottom part of the film, unaffected by plasma, in chloroform vapour. It also plays the role of a barrier for chloroform vapour which therefore can diffuse into the PDMS film only from any remaining exposed surfaces. The different degree of swelling of the top and the bottom layers of the films might also contribute to the generation of bending moments in the course of tube formation. The access of vapour to the interior of the film was facilitated by making a slit in the film, either by mechanical cutting, or via UV laser ablation of the polymer. After closing the recepticle, containing chloroform vapor, the tube’s formation was observed during the course of a few minutes. An SEM image of a typical PDMS tube formed is shown in figure 1b. In well-formed tubes without defects, the consecutive layers tightly approach each other and form into tube walls that are impermeable to liquids.

Connection of PDMS tubes to external pumping systems. The rolled-up PDMS tubes were connected to an external micropump system and the flow of fluids through the tubes was successfully demonstrated. A simple microfluidic device was designed as shown in figure 2a. The same figure demonstrates schematically the integration of a tube with a simple electronic circuit, such as a V-shaped electrode track, partially encased in the tube. In this case, the tubes did not detach from the glass substrate. Their connection to the external tubings and the micropumps was realised by small blocks of PDMS with a special profile.

Control of the rate of a chemiluminescent reaction inside the capillary by an encased electrical circuit. The possibility to directly integrate electrical and microfluidics circuits, achieved via encasing of the 2D electrical circuits formed on the surface of a scrollable film, is one of the most interesting aspects of the current approach. The encased circuits can be used for the generation of temperature profiles [14] or electromagnetic fields inside the capillaries. In the present work, we demonstrate the formation of localized temperature gradients inside the capillaries so as to exercise temperature control of the rate of a chemiluminescent reaction inside of the PDMS microcapillary. To this end, V-shaped electrodes were formed on top of the PDMS films by silver ink and rolled up (figure 2b). A solution, taken from a commercial chemiluminescent light stick (mixture of solutions of phenyl oxalate ester, hydrogen peroxide, and a fluorescent dye), was injected into the tube via the tube connections. A source of DC electrical current was connected to the electrode via the contact pads. Due to the high surface to volume ratio of the tubes, heat was quickly dissipated to the environment, leading to a strong localization of the elevated temperature and intense light emission at the encased parts of the electrodes. The intensity of the reaction can be varied by the applied voltage.

CONCLUSION
Micro-capillaries produced by the self-rolling of thin oxidized layers of poly(dimethyl siloxane) were obtained and analysed as prospective elements of microfluidics circuits. The rolling of the films is due to inhomogeneous swelling of a thin PDMS layer in a saturated vapour of chloroform, which induced a differential transverse stress profile and resulted in a high upward bending moment in the film, caused film detachment and subsequent rolling. The microcapillaries with high aspect ratio were integrated in microfluidic circuits and circulation of colored water in them was demonstrated. V-shaped electrodes, formed on the surface of the PDMS films with silver nanoparticles, were transformed in sub-millimeter out-of-plane solenoidal structures during the course of tube formation. These structures were explored as micro-resistors for local heating of the tube’s interior. Heat release was visualized via light intensity emitted in the course of a chemiluminescent reaction inside the tube. The entire inner surface of the capillaries could be contacted by the elements
of the circuits, and not only the side adjacent to the substrate, as in the case for more traditional approaches to formation of the microfluidics devices. This feature can be exploited to generate more homogeneous temperature fields.

**Figure 2:** (A) The scheme of a PDMS tube integrated with microfluidics and electronics circuits. (B) SEM image of one extremity of a self-rolled PDMS tube. (B) Chemiluminescent reaction in the PDMS microtube with and without Joule heating of the tube by the encased electrode. Scale bar: 1cm.

or fields which have more complex 3D geometry, than those generated by planar circuits. The fact that micro-solenoids obtained by self-rolling are co-axial with the tubes around which they are wound deserves special interest. In theory this permits to generate intra-tubular magnetic field configurations which are not feasible when using planar electrical circuits on the substrates. This result is important for the growing field unifying magnetism and microfluidics [15].

The use of PDMS for a microtube`s fabrication allows to explore the numerous advantageous characteristics of this material, such as high temperature and chemical stability, optical transparency, and biocompatibility. The tubes can be easily integrated in a PDMS matrix, or joined to external pumping systems via PDMS connectors. The elasticity of the tubes greatly facilitates operations with them, since there is no risk of their accidental breaking. The gas permeability of PDMS makes the capillaries formed from this material suitable for experiments with single living cells which need sufficient oxygenation.

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