Electronic supplementary information

Experimental details

1.1. Materials and methods

PDMS samples for tensile measurements and IR characterization were prepared mixing the polymer base and the curing agent (Sylgard 184, Dow Corning) with different weight ratios (5:1, 10:1, 20:1, and 30:1) and degassing in low vacuum for 1 h. The mixture was then poured into 2 cm × 1 cm × 1 mm PMMA molds (fabricated by milling machine) and cured in a convection oven for 1 h at 70 °C.
The same compositions have been used to fabricate membranes by spin coating the degased PDMS mixture onto PMMA foils (1 mm thick). We choose to work with PMMA instead of standard glass or silicon substrates since reducing the PDMS mixing ratio the adhesion strength of the cross-linked material with Si-like surfaces became stronger and release agents are needed in order to detach the self-standing membrane for permeability measurements.
PMMA foils were cut into 2 cm × 2 cm pieces and then rinsed with isopropyl alcohol in an ultrasonic bath for 10 min. The PDMS mixture was spin coated in order to obtain thicknesses in the range 10 - 40 μm (measured by profilometry with P.10 KLA-Tencor Profiler) and crosslinked at 70 °C for 20 minutes on hot plate. This soft curing step was performed to allow a partial crosslinking of the material, that produces the a soft hardening of the membrane. As already reported by Wu et al. [S1] this strategy allows to facilitate the subsequent bonding of the membrane with other PDMS components, as described below. The area of the membrane was define by manual cutting 5 mm × 5 mm pieces.
The PDMS membrane was assembled following the experimental set up depict in Figure 2a and b. 10:1 PDMS was used to replicate a PMMA microfluidic pattern (fabricated by milling machine) designed for the permeability experiments. The microchannel is 0.3 mm wide and 0.05 mm high.
The obtained microfluidic cover chip was manually assembled on top of a glass substrate exploiting the bonding . Briefly a thin layer of PDMS mixture was spun on a glass slice and then selectively transferred to the microfluidic chip using a stamping process. The chip was then bonded to the glass surface by thermal treatment at 70°C for 30 min.
The partially cross-linked PDMS membrane was bonded at the outlet of the microfluidic by a thermal treatment at 70°C for 30 min while the homemade PDMS interconnection was bonded on top of PDMS membrane exploiting the same “stamp and stick” method as before. The resulting device is a dead-ended microfluidic channel. A conveniently designed PMMA ring was used to avoid gas leakages when a PE tube was connected to the PDMS interconnection (see Figure S1).
Overall, taking into account all the thermal steps of the process, the PDMS membrane undergoes a heat treatment of 20 minutes after the spin coating, other 30 minutes during the bonding to the device outlet port and other 30 minutes during the bonding of the interconnection to the membrane, for a total of 1 hour and 20 minutes at 70 °C, energy dose comparable with many other works published so far on PDMS cross-linking [S2-S5]. At the end of the manufacturing process the devices have been stored overnight at room temperature (18 hours at 25 ° C) before the permeability testes.

Figure S2 show the 3D cross-sectional view of the microfluidic device for permeability measurements with geometrical dimension.

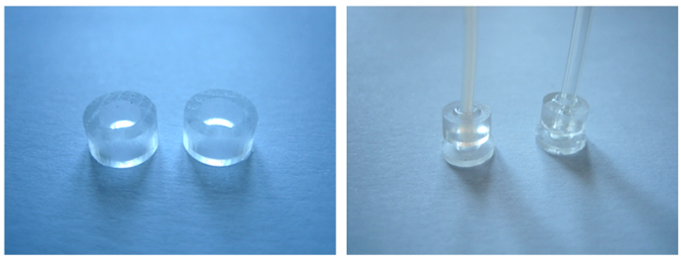

Figure S1. Digital photograph of PMMA ring

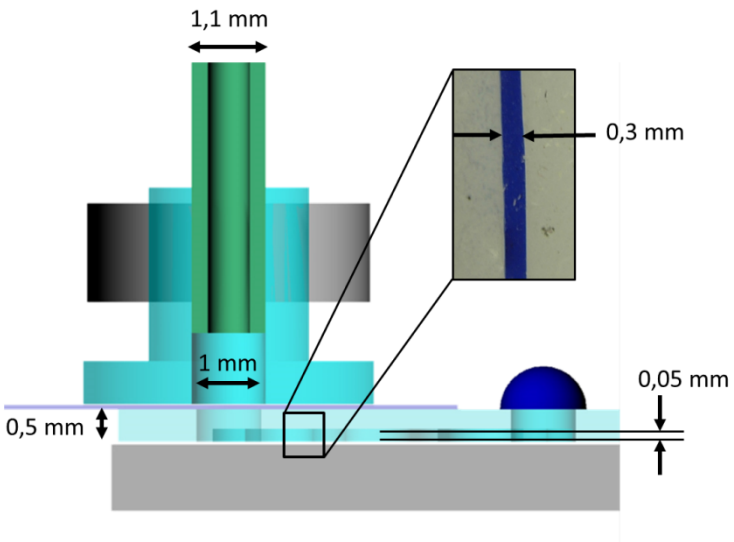

Figure S2. 3D cross-sectional view of the microfluidic device for permeability measurements with geometrical dimension in the real experimental condition.

1.2. Characterization techniques

Fourier transformed infrared (FTIR) spectra were recorded using a Nicolet 5700 FTIR Spectrometer used in attenuated total reflectance (ATR) mode with 4 cm^{-1} resolution and an average of 64 scans. FTIR was performed on PDMS substrates to examine the dependence of material composition on different mixing ratios.

The mechanical properties were investigated by tensile measurements made using a Instron-3366 instrument equipped with an electromechanical extensimeter (clip gauge); an initial strain rate of 5 mm/min was adopted. Data were elaborated by the Instron software. At least five specimens for each measurement were tested.

The molecular weight between cross-links (Mc) was calculated as describe by previous researches.

The fluidic characterization setup, depict in Figure 2b, consisted on a syringe pump connected, through a 'T' joint, to both a commercial pressure transducer (26PCFFA6G Honeywell) and the PDMS interconnection via LDPE tubing. Pressure data vs time were recorded through a multimeter unit (Agilent Technology 34970A) interfaced to a PC. The flow rate was measured by optical evaluation of the microchannel length filled by water under negative pressure.

In order to allow the pressure setting during the microfluidic permeation experiments a calibration step was performed taking into account the length and the size of tubing between the various components. The commercial pressure transducer (26PCFFA6G Honeywell) has been connected with the same tubing used during flow-rate measurements to a analogic pressure gauge linked to the Nitrogen line. The sensor was powered by a DC power supply (GW INSTEK GPS-4303) and pressure data were recorded through a multimeter unit (Agilent Technology 34970A) interfaced to a PC. The sensor was biased at 12V with sampling rate equal to 1 second varying the pressure in the range 0.5 -2,5 bar with steps of 0.5 bar.

1.3 FEM simulation

The Finite Element Method (FEM) simulations were carried out implementing the structural mechanics module of the software COMSOL Multi-physics 4.3b. The modelling of the PDMS membrane mechanical response, although approximate, has allowed the quantitative estimation of the area and thickness of the membranes under deformation needed to calculate the permeability coefficients.

Table S1. Area and thickness values of pressurized PDMS membrane (20 μm thick) obtained by FEM simulation for the three composition under investigation and the calculated permeability values.

PDMS MR	p_2-p_1 (bar)	Membrane area (mm^2)	Membrane thickness (μm)	Permeability (Barrer)
5:1	0	0.78	20	-
	0.25	0.99	15.85	61.5
	0.5	1.09	14.44	90
	0.75	1.16	13.53	131
10:1	0	0.78	20	-
	0.25	1.04	15.09	270
	0.5	1.15	13.65	526
	0.75	1.23	12.76	573
20:1	0	0.78	20	-
	0.25	1.13	13.89	950
	0.5	1.24	12.66	1670
	0.75	1.37	11.45	1502

The FEM simulation has been implemented on a geometry that represents the actual geometrical dimensions of the device experimentally fabricated. The graphical representation of the membrane displacement and stress induced by the pressure difference (reported in Figure 4a) does not show the other components of the device because they are not interested in mechanical deformation. In fact, the microfluidic chip bonded to the glass and the interconnection have been considered as physical constraints, as well as the membrane fraction bonded between them. The only part subjected to deformation is the fraction of the membrane free from constraints.

References

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