

Supplementary Materials

Fluorescent citric acid-modified silicone materials

Wiktor Kasprzyk, Piotr Krzywda, Szczepan Bednarz and Dariusz Bogdał

Experimental

Citric acid (CA), poly(dimethylsiloxane) (PDMS), tetraethoxysilane (TEOS), N-[3-(Trimethoxysilyl)propyl]ethylenediamine (TMS) and dibutyltin dilaurate (DDC) were supplied by Sigma-Aldrich. Tetrahydrofuran, n-heptane, potassium dichromate and iron(III) nitrate were supplied by POCH (Poland). Ethanol 99.8% and acetone were supplied by Chempur (Poland). Phthalate buffer pH 4.01 and borax buffer pH 9,18 were supplied by LabStand (Poland). Ascorbic acid was supplied by Polfa (Poland).

Synthesis of FSM modified in total volume

1,65 g PDMS (750 cSt), 0,858 cm³ TEOS and 25 μl TMS were mixed in vial by magnetic stirrer. Then 25 μl of DDC was added and mixed again. Next, the mixture was poured into polyethylene forms and left in laboratory oven at 50°C for 24 h. After crosslinking of the polymer, it was cut into two pieces (A and B at Fig. S1). A was immersed in THF solution of CA (10 %) for 5 minutes while B was a control sample. Then both materials were heated at 100°C for 2 h, washed with distilled water for 24 h and vacuum dried. Unmodified silicone material was prepared according to above protocol but without TMS addition.

Furthermore, the local fluorescence of the material could be obtained via covering of the specific part of TMS-modified material with CA solution in THF and further heating at 100°C for 2 h. After washing in distilled water and drying the local fluorescence could be observed under UV light (365 nm).

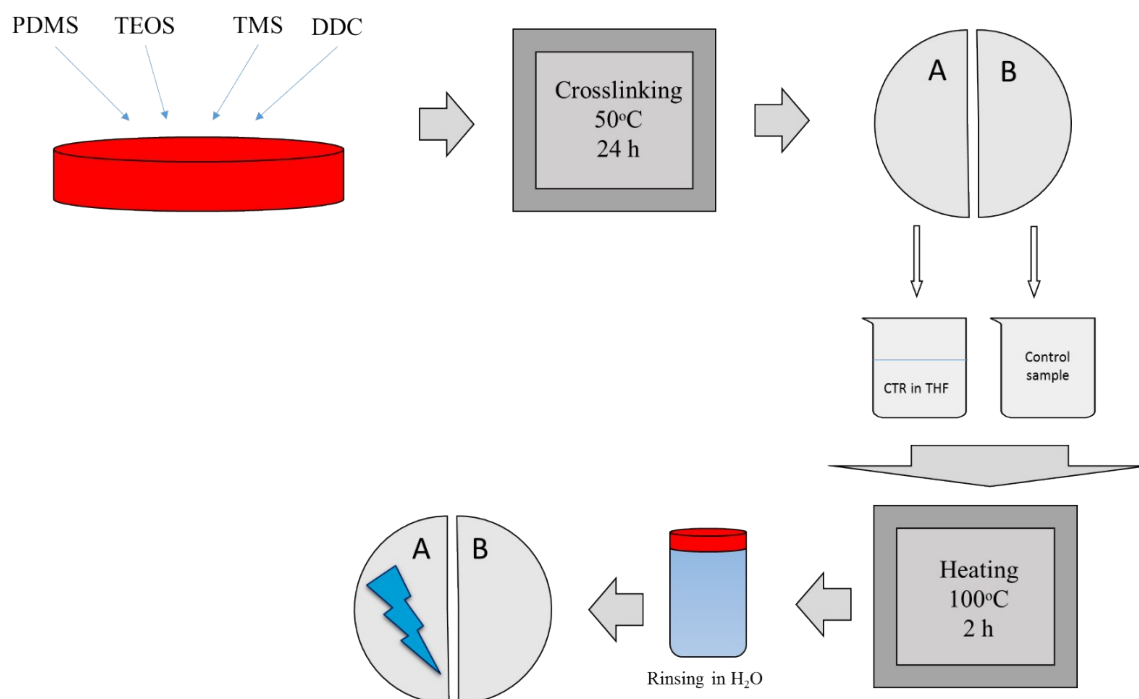


Figure S1 Synthetic scheme of the synthesis of FSM modified in total volume.

Synthesis of surface modified FSM

1,65 g PDMS (750 cSt) and 0,885 cm³ TEOS were mixed in vial by magnetic stirrer. Then 25 µl of DDC was added and mixed again. Next, the mixture was poured into polyethylene forms and left in laboratory oven at 23°C for 24 h. Afterwards, pre-crosslinked silicone matrix was immersed in ethanol solution of TMS (15 %) for 5 minutes and then cross-linked at 50°C for another 24 h. Then material was washed with distilled water for 24 h and cut into two pieces (A and B at Fig. S2). A was immersed in THF solution of CA (10 %) for 5 minutes while B was a control sample. Then materials were heated at 100°C for 2 h, washed with distilled water for 24 h and vacuum dried.

Local modification of the material was obtained via covering of the specific location of pre-crosslinked silicone with TMS solution and further cross-linking at 50°C for 24 h. Then the material was washed with distilled water and vacuum dried. Afterwards the fluorescent symbols could be developed by immersion of the material in CA solution, drying in 100°C for 2h, rinsing in water and observation under UV light (365 nm).

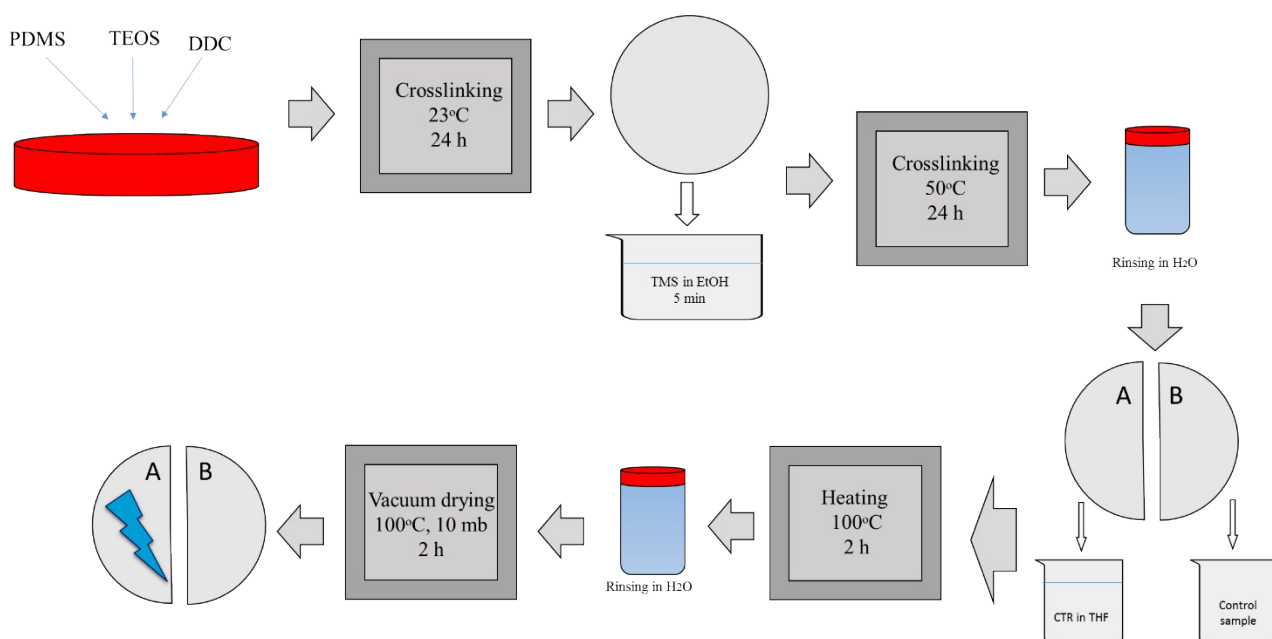


Figure S2 Synthetic scheme of surface modified FSM.

Characterization

The FT-IR spectra were acquired using FTIR-i10 NICOLET ThermoScientific spectrophotometer with ATR attachment. The emission spectra of FSM were acquired using Ocean Optics MINI-D2 spectrofluorimeter (excitation 365 nm by Spectroline ENF-260C/FE portable UV lamp). Measurements were carried out on a strip of material which was cut to fit the dimensions of a wall of a 4 ml quartz cuvette. Then the strip of material was fixed on the inner surface of cuvette's wall and placed in cuvette holder of the spectrofluorimeter. The fluorescent measurements of the materials were conducted by filling the cuvette with various solutions. Contact angle measurements were vested according to photographs obtained by MOK z0010 camera. Distilled water was used as the probing liquid. UV/VIS absorption spectra of Fe^{3+} and $\text{Cr}_2\text{O}_7^{2-}$ solutions were taken on a PG Instruments Ltd P80+ spectrophotometer.