Electronic Supplementary Materials *Mendeleev Commun.*, 2026, **36**, 308–310

Self-healing ‘siloxane equilibrium’ materials after low-power electric breakdown in small-volume cells

Aleksandr V. Prokudin, Mikhail A. Dziuba, Valery I. Safonov, Konstantin V. Deriabin, Anna S. Miroshnichenko, Regina M. Islamova, Ekaterina V. Bartashevich and Anton V. Korzhov

Contents

S1. Supplementary experimental section

S1.1. Materials

Octamethylcyclotetrasiloxane (D_4, 98%) and 25 wt.% tetramethylammonium hydroxide (TMAH) solution in methanol were purchased from Abcr GmbH (Karlsruhe, Germany) and used as received. A bicyclic monomer, 1,3-*bis*(2-(2,4,4,6,6,8,8-heptamethyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxan-2-yl)ethyl)-1,1,3,3-tetramethyldisiloxane (bis-D_4), was synthesized by hydrosilylation reaction between 1,1,3,3-tetramethyl-1,3-divinyldisiloxane (98%, Abcr GmbH, Karlsruhe, Germany) and 1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane (95%, Abcr GmbH, Karlsruhe, Germany) using platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex 0.1 M solution in xylene as a catalyst according to the reported method.[S1] The structure of the described substances was confirmed by ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ nuclear magnetic resonance spectroscopy before being used (**Figures S1–S2**). All NMR spectra are consistent with the literature data.[S1–S4]

S1.2. Preparation of SHSR

SHSR was obtained by a cross-linking anionic ring-opening copolymerization of D_4 and bis-D_4 using TMAH as an initiator (see **Fig. 1**) similar to the refs.[S1–S4] The bulk polymerization with further cross-linking was conducted by mixing bis-D_4 (25.0 mg) with D_4 (5.00 g) and TMAH (≈2.0 mg) in a round-bottom flask under argon at 100 °C. The concentration of the cross-linking agent (bis-D_4) was ≈0.5 wt%. The reaction mixture was sealed and stirred at 100 °C for 10–15 min. The formed viscous gel was poured into a polytetrafluoroethylene (PTFE) mold and then cross-linked at 100 °C for 24 h. The obtained SHSR films with a thickness of ≈1 mm were peeled off the PTFE mold and cut out to obtain shapes according to the requirements of further experiments. The as-prepared SHSR was a thick transparent gel, which has an ability to self-heal at r.t. by the mechanism of "siloxane equilibrium".[S1–S4] The structure of SHSR was confirmed by NMR spectroscopy (**Figure S3**) and consistent with ref.[S1]

S1.3. NMR data

NMR spectra were obtained using a Bruker Avance III 400 spectrometer (Bruker, Santa Barbara, CA, USA) in $CDCl_3$ at r.t. operating at 400 MHz for ^{1}H, 100 MHz for ^{13}C, and 80 MHz for ^{29}Si NMR, respectively. The $^{13}C\{^1H\}$ NMR spectra were recorded with ^{1}H decoupling. Chemical shifts of signals are shown in δ-values [ppm] referenced to the residual signals of $CHCl_3$ and neat $(CH_3)_4Si$: $\delta = 7.26$ (^{1}H), 77.2 ($^{13}C\{^1H\}$), and 0.0 ppm ($^{29}Si\{^1H\}$).

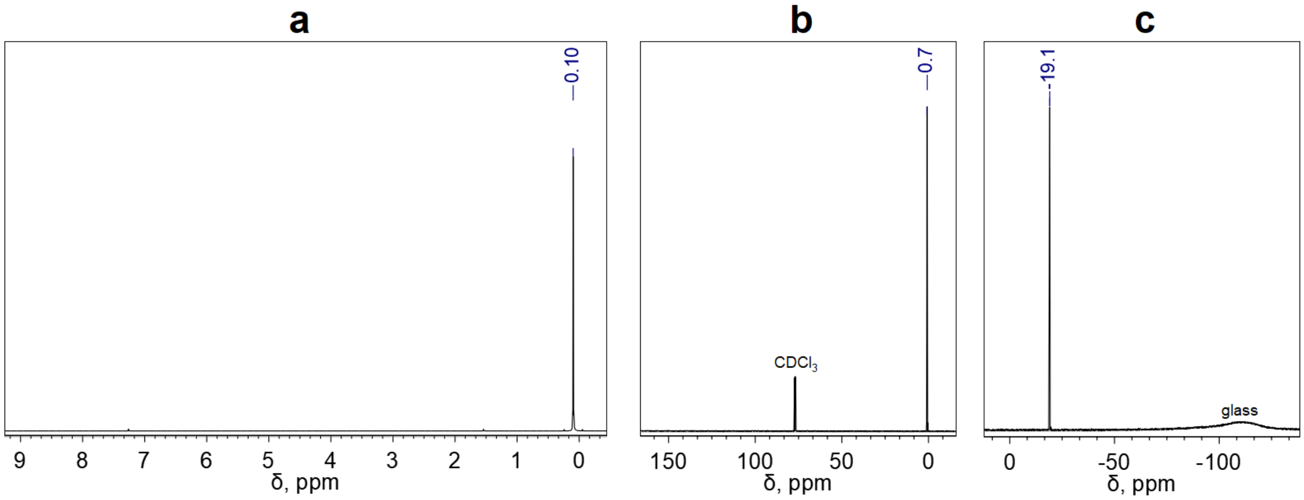

Figure S1. ^{1}H (**a**), $^{13}C\{^1H\}$ (**b**), and $^{29}Si\{^1H\}$ NMR spectra (**c**) of D_4 in $CDCl_3$.

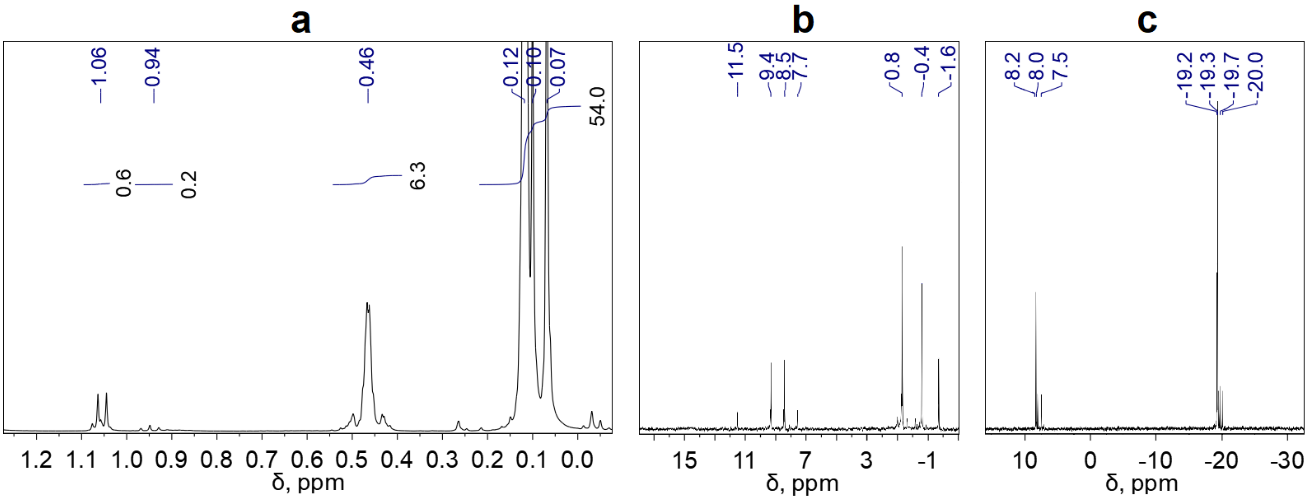

Figure S2. ^{1}H (**a**), $^{13}C\{^1H\}$ (**b**), and $^{29}Si\{^1H\}$ NMR spectra (**c**) of bis-D_4 in $CDCl_3$.

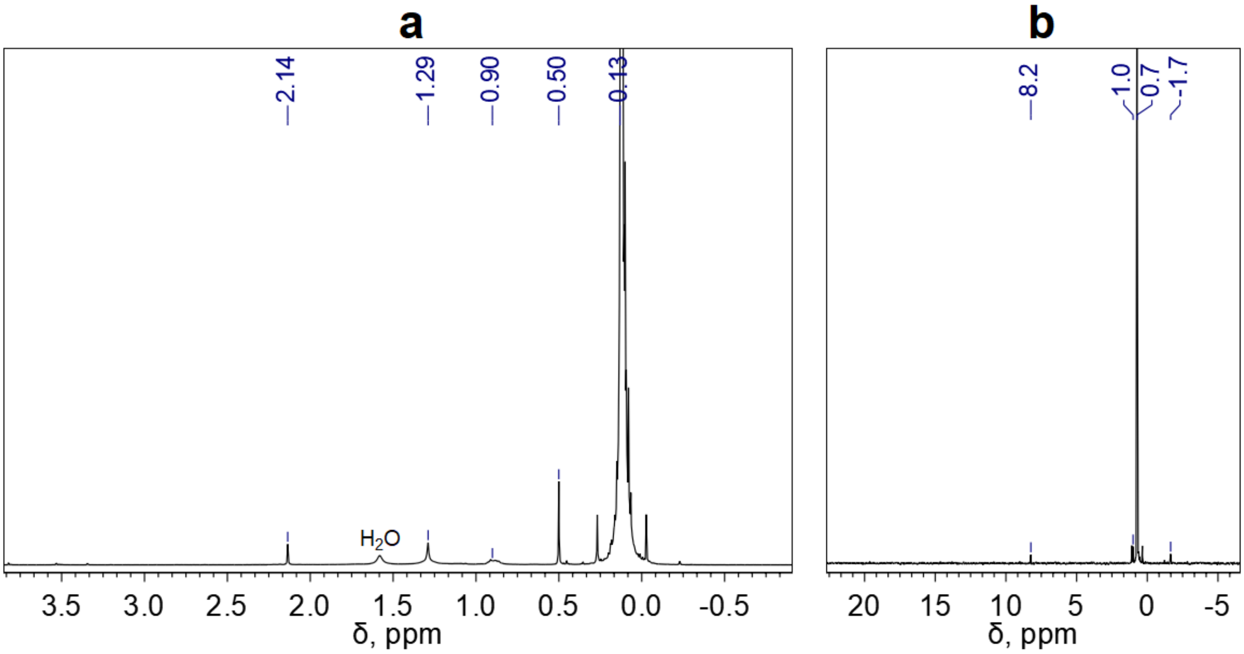

Figure S3. ^{1}H (**a**) and $^{13}\text{C}\{^{1}\text{H}\}$ (**b**) NMR spectra (**c**) of soluble fraction of SHSR in CDCl$_3$.

S1.4. Electrical breakdown experiments

The experimental setup incorporated a SKAT-70M DC power supply (Industrial Equipment Plant SKAT LLC, 2021, product details available at https://skat-v.com/product/skat-70m) with a maximum output of 10 kV for controlled high-voltage application (**Figure S4**). To mitigate damage to the polymer sample during EB, a 100 MΩ current-limiting resistor (rated for 10 kV) was integrated into the test cell circuit in series configuration. Transient current surges occurring at the instant of breakdown were quantified using a PA1 microammeter (One Scientific Instruments, Russia). The electrodes, encapsulated within high dielectric-strength polymer insulation, were precision-aligned and secured between polypropylene bars affixed to a glass substrate. A standardized interelectrode gap of 1.0 mm was established using calibrated spacers. This configuration reliably accommodated sample volumes as low as 0.03 mL and allowed avoiding breakdown on the surface of an analyzed sample and inside the frame channel.

The high-voltage supply was manually disengaged immediately following each breakdown event to prevent sustained electrical stress. The interelectrode space was monitored *via* an Orbita OT-INL40 USB microscope (Chongqing Dontop Optics Co., Ltd, Beibu New District, Chongqing, China) with the varifocal lens and built-in illuminated stage. To ensure experimental consistency, the microscope's optical alignment was stabilized using a fixed stage-lens configuration throughout testing.

Five cuvettes were fabricated. Samples were cast, cured, inspected microscopically for inclusions, and equilibrated for 24 h under controlled conditions prior to testing. Dielectric strength was evaluated in duplicate for all five specimens: initially following sample fabrication and subsequently upon complete visual resolution of defects induced by the primary EB event. Testing occurred under controlled ambient conditions (r.t., relative humidity of 61±5%), with a VIT-1 hygrometer (Moscow region, Russia) tracking environmental parameters. Confidence intervals for direct measurements were calculated using Student's *t*-distribution (to account for random errors) with a 95% confidence level.

According to the ref.,[S5] the convergence and contact of surfaces include into the initial stage of the self-healing process. The self-healing efficiency at this stage was monitored using measurements of the linear dimensions of the defect, obtained by processing photographs of the defect. Measurements of the linear dimensions of the defect were conducted with a periodicity of 1 h from the moment of defect formation until its visual disappearance.

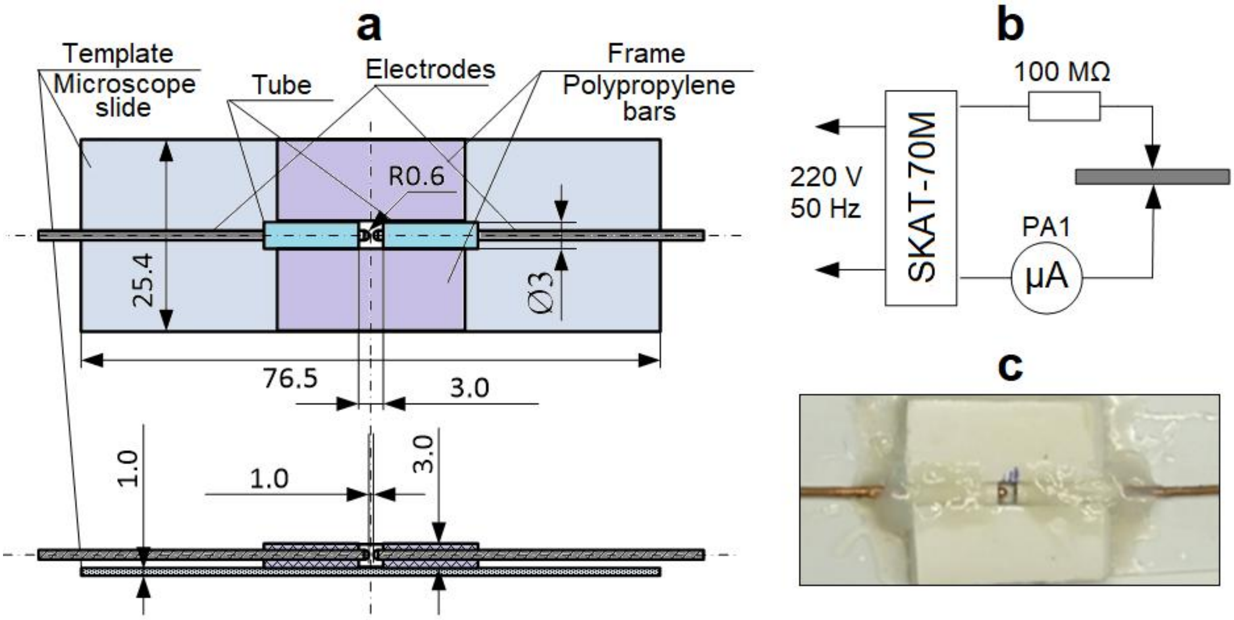

Figure S4. Principal scheme (a), electrical circuitry (b) and photograph (c) of the EB testing set. Geometrical parameters are given in mm. The specific electrical voltage at first breakdown (E_{BD1}) for SHSR films was determined using SKAT-70M DC as a power supply.

S2. References

S1 A. A. Rashevskii, K. V. Deriabin, E. K. Parshina and R. M. Islamova, *Coatings*, 2023, **13**, 1282; https://doi.org/10.3390/coatings13071282.

S2 P. Zheng and T. J. McCarthy, *J. Am. Chem. Soc.*, 2012, **134**, 2024; https://doi.org/10.1021/ja2113257.

S3 W. Schmolke, N. Perner and S. Seiffert, *Macromolecules*, 2015, **48**, 8781; https://doi.org/10.1021/acs.macromol.5b01666.

S4 Y. E. Moskalenko, V. Bagutski and C. M. Thiele, *Chem. Commun.*, 2017, **53**, 95; https://doi.org/10.1039/C6CC08762K.

S5 R. P. Wool and K. M. O'Connor, *J. Appl. Phys.*, 1981, **52**, 5953; https://doi.org/10.1063/1.328526.