Experimental section

1. Characterization techniques

Bulk density was calculated from the mass and volume of the cylindrical aerogels. The skeletal density was measured using a helium pycnometer (AccuPyc II 1340, Micromeritics, USA). An FEI TECNAI F20 field emission transmission electron microscope (TEM), operated at an accelerating voltage of 200 kV, was used for detailed microstructural investigation of the aerogel networks and for element-specific energy-filtered analysis (EFTEM). Scanning electron microscope (SEM) images were taken using a Zeiss ULTRA Plus microscope at 5-10 kV with an in-lens detector and working distance of 3 mm. Energy-dispersive X-ray (EDX) spectra were collected in the SEM using an X-Max silicon drift detector. Fourier transform infrared spectroscopy (FTIR) were obtained by a Bruker Vertex 70 with a 4 cm$^{-1}$ resolution and scan range 400 to 4000 cm$^{-1}$. Nitrogen adsorption-desorption measurements were carried out at 77 K using a Micromeritics ASAP 2420 Accelerated Surface Area and Porosimetry System. Before analysis, the sample was outgassed at 60 °C in vacuum (10–5 bar) for 24 h, to remove adsorbed species. The specific surface area was calculated applying the Brunauer, Emmett and Teller 5-point method in the relative pressure range of $p/p_0 = 0.05–0.3$. From the skeleton and bulk density values, the porosity $\varepsilon$ (%), pore volume ($V_p$) and pore diameter ($D_p$) of the samples were calculated through equations S1, S2, and S3, respectively.

$$\varepsilon(\%) = \frac{1/\rho_b - 1/\rho_s}{1/\rho_b} \times 100 \quad (S1)$$

$$V_{pore} \left( \text{cm}^3/\text{g} \right) = \frac{1}{\rho_b} - \frac{1}{\rho_s} \quad (S2)$$
\[ D_{\text{pore}}(\text{nm}) = \frac{4V_p}{S_{\text{BET}}} \]  

(S3)

Solid-state $^{29}$Si-, $^{13}$C- and $^1$H- nuclear magnetic resonance (NMR) spectra of the aerogels were obtained by using a Varian Inova 500 spectrometer using a 4 mm solids probe with cross-polarization and magic-angle-spinning (MAS) at 11 kHz. A solid-state $^1$H–$^{29}$Si heteronuclear correlation spectrum was collected using 4 mm zirconia rotors with a spinning rate of 11 kHz and applying homonuclear decoupling using continuous phase modulation (DUMBO) to increase the $^1$H spectral resolution.

Mechanical characterization of the composites was carried out on monolithic cylindrical samples using a Zwick Roell Z010 cLine universal testing machine (UTM) equipped with a 1 kN force transducer (KAP-S, AST Gruppe GmbH, Germany) in a controlled environment (23 °C, 50% relative humidity). Stress-strain curves were plotted in compression mode, and elastic moduli were calculated from the linear range of the curves which typically occurred at 3 ± 1% strain. A constant deformation rate of 0.5 mm/min was used, and the maximum strength was taken at the first signs of buckling which occurred typically at >70% strain. The surface wettability of PMSQ-SF aerogel sample was tested by a contact angle analyzer (FM40 Easy Drop KRUSS). The thermal conductivity of the PMSQ-SF aerogels was measured using a transient method (Thermal constants analyzer TPS 2500 S, Hot Disk). The sensor is clamped between two identical disc-shaped pieces of the sample, which have a diameter and thickness of 1 cm (properly cut from the cylindrical aerogel samples). This analysis was carried out at 20 °C and the equipment presents a reproducibility and accuracy over 1% and 5%, respectively.

1.2 Measurement of oil / organic solvent absorption capacity

A cylindrical piece of PMSQ-SF aerogel (6 mm (diameter) × 6 mm (length)) were prepared by punching the initial sample and immersed in different oils and organic solvents at room temperature. The sample was taken out of the oils/ solvents after 10 min, the excess of oil/ solvent removed with filter paper for several seconds. The oil/ solvent absorption capacity of the sample was determined by weighing the sample before and after absorption and calculated according to the following equation:

\[ \text{Absorption capacity} = \frac{m_t - m_i}{m_i} \times 100\%, \]
Where $m_i$ and $m_f$ were the weight of the PMSQ-SF aerogel before and after absorption, respectively.

### 1.3 Reusability, gravity-driven and continuous oil/water separation

To testify the reusability of PMSQ-SF aerogel as absorbents, absorption-recovery cycle tests (5 cycles) of the aerogels were performed using methanol and acetone as solvent. The solvent filled PMSQ-SF aerogel was very gently squeezed with a tweezer and then dried at room temperature (0.5 h) for reuse.

For the gravity-driven test, a mixture of oil (vegetable oil) and water (dyed with MB) is prepared. A cylindrical piece of aerogel 15 mm in diameter and 30 mm in length was placed into the glass tube with the same inner diameter as that of aerogel cylinder. When the oil-water mixture solution was filtered through the aerogel, water was removed, and the clean vegetable oil was filtered/collected in the aerogel inside the test tube. Furthermore, a simple oil-water separation device was designed in order to investigate the possibilities of continuous removal of oil from the oil-water mixture. In principle, a silicone tube was fixed in one end to the round bottom flask (receiver), which was connected to a vacuum pump, and with the other end, it was connected to an aerogel piece (10 mm (diameter) × 10mm (length)) by means of a micropipette tip. The PMSQ-SF aerogel was immersed into the oil-water mixture and then the cleaned water was continuously pump into the container while the oil was trapped inside the aerogel.
Fig. S1 SEM micrographs of [Si]$_{3.5}$ hybrid aerogel series in different magnification.
Fig. S2 SEM micrographs of [Si]_{17.5} hybrid aerogel series.

Fig. S3 Different possible chemical interactions of the carboxylic acid-modified PMSQ network with silk fibroin.
Fig. S4 ATR-FT IR spectroscopy of PMSQ-SF aerogels hybrids with (a) and (b) without TMSPM coupling agent. EM refers to pure PMSQ aerogels.

Fig. S5 N₂ adsorption-desorption isotherms of selected PMSQ-SF aerogels.
Fig. S6 Power-law relationship between density and modulus, (a) [Si]_{3.5}, (b) [Si]_{17.5}.
Fig. S7 TG-DTA curves of $[\text{Si}]_{3.5}$ PMSQ-SF hybrid aerogels.
Fig. S8 Absorption kinetics of vegetable oil onto the PMSQ-SF aerogels at 23 °C.
Fig. S9 (a) Pseudo first order and (b) Pseudo-second order absorption linear fitting of vegetable oil onto the PMSQ-SF aerogels at 23 °C.
Fig. S10 UV-Vis spectra of oil red O in vegetable oil and the 5th filtrate.

Table S1. Sample behavior after exposing to the harsh condition.

| Sample   | Sample initial weight (g) | Sample weight (g) after successive exposing to LN₂ (1 min) and 100 °C (1 hr) | Compressive strength (MPa) |
|----------|---------------------------|-------------------------------------------------------------------------------|----------------------------|
| SF       | 0.05 ± 0.002              | 0.05 ± 0.001                                                                 | 0.31                       |
| EM-SF-40 | 0.21 ± 0.004              | 0.20 ± 0.004                                                                 | 2.5                        |

Fig. S11 Burning behavior of the SF aerogel with time.