

Supporting Information

Synergistic Enhancement of Thermomechanical Properties and Oxidation Resistance in Aligned Co-Continuous Carbon-Ceramic Hybrid Fibers

Jakob Denk,^a Xiaojian Liao,^{†bc} Martin Dulle,^d Stefan Schafföner,^a Stephan Förster,^d
Andreas Greiner,^b Günter Motz,^{*a} Seema Agarwal,^{*b}*

E-mail: agarwal@uni-bayreuth.de (S. Agarwal); guenter.motz@uni-bayreuth.de (G. Motz);
xj_liao24@tju.edu.cn (X. Liao)

EXPERIMENTAL SECTION

Materials: Polyacrylonitrile copolymer (PAN, copolymer with max. 8 % methyl acrylate and methallylsulfonate according to the datasheet from Dolan GmbH; number average molar mass (M_n) = 95,000; registration No. 26658-88-8) was obtained from Dolan GmbH (Germany). Oligosilazane Durazane 1800 (OSZ) was obtained from Merck (Germany). Dicumylperoxide (DCP) was obtained from Sigma-Aldrich (Germany). N, N'-dimethylformamide 99.99 % (DMF) from Fisher Scientific GmbH (Germany) and anhydrous toluene from Carl Roth (Germany), were obtained. All chemicals were used as received.

Wet-spinning of Polymer fibers: The spinning solution was prepared by dissolving PAN powder and Durazane1800 with 3 wt.% DCP in DMF overnight at room temperature (**Table S1**). Afterwards, the viscous solution was filled into a 10 mL metal syringe and stored for 8 h until all air bubbles had risen to the top of the syringe resulting in a bubble-free solution. A custom-made wet-spin setup, including a syringe pump, precipitation bath, and tube furnace, was assembled to spin continuous polymer fibers from the PAN/OSZ hybrid precursors solution. The syringe pump was used to control the flow rate of the spinning solution, while the precipitation bath facilitated the formation of gel fibers, and the furnace oven allowed for controlled heating for stretching and consolidating the fibers. For the spinning process, 30 G needles with a flat tip (inner diameter: 190 μm) and a middle-pressure syringe pump (NEMESYS cetoni, Germany) were used. The pump was programmed to the required flow rate (0.0006-0.001 ml s^{-1}) in the associated software and the polymer solutions were spun into the precipitation bath at room temperature. For the PAN/OSZ-40 fibers, 30 vol% DMF, for PAN/OSZ-20 fiber, 20 vol% DMF and for pure PAN fibers, dist. water with 20 vol% DMF was used as the precipitation bath (**Table S1**).

The single continuous polymer fiber obtained was collected and stretched by a custom-made stretching instrument consisting of three parts: a tubular furnace with one heat zone (Heraeus, D6450 Hanau, Typ: RE 1.1, 400 mm length, Germany), two rollers controlled by electronic motors and a laptop with "LV2016" software, which was used to precisely control the velocities of the motors. The fibers could be stretched continuously by adjusting the velocities of the two rollers in the LV2016 software. The SR was calculated by the equation: $\text{SR} = V_f / V_s$, where V_f and V_s represent the velocities of the fast roller and slow roller, respectively, similar to previously published literature from our group.¹ To obtain a high SR (5-

9), the fibers were repeatedly stretched while heated to 130 °C and dried for four days in a vacuum drying furnace (Heraeus, VT 6060 M) at 70 °C.

Stabilization and pyrolysis to non-continuous C/SiCNO fibers: For non-continuous stabilization and pyrolysis of the fibers, the fibers were bundled in rovings of 25 fibers and attached to graphite pieces using a high-temperature mullite adhesive (Porrathin 30, Rath, Austria). This method of attachment allowed the fibers to shrink and contract without tearing apart. Stabilization was performed using a stepwise temperature program from RT to 250 °C (Figure S1) in an oxide-lined furnace under atmospheric pressure (Nabertherm N41/H, Germany). Pyrolysis proceeded in a tube furnace (Thermal Technology, High-Temperature TA 106320, USA) at 1000, 1200, 1350, 1500 °C (heating rate 3 K min⁻¹, 1 h hold time at maximum) under atmospheric pressure and N₂ atmosphere (flow rate 15 L/h).

Stabilization and pyrolysis to continuous C/SiCNO fibers: For continuous production, eight fibers were combined into a bundle. The bundles were stabilized continuously under tension, atmospheric pressure, and air atmosphere in a custom-made tubular furnace with three heating zones (380 mm in one heating zone length). A carefully designed three-step heating program was implemented during the stabilization process to gradually increase the temperature. In the first step (I), temperatures were set at 130-150-170 °C; in the second step (II), temperatures were raised to 190-210-230 °C; and finally, in the third step (III), temperatures reached 230-250-250 °C. The fiber collecting rate was about 380 mm/h. Subsequently, pyrolysis also took place continuously under tension, atmospheric pressure, and N₂ atmosphere at 1200 °C (Nabertherm RHTC 80-710/15, Germany). The gas flow rate was set to 250 ml/min. After pyrolysis, the fiber was cut into smaller pieces for the analytical measurements.

Scanning electron microscopy: The SEM images of the nanofibers were acquired with a Zeiss Sigma 300 VP (Gemini 2, Germany) scanning electron microscope equipped with a field emission cathode, a secondary electron (SE2), and an inlens detector. An acceleration voltage of 3 kV and a working distance of about 5 mm was used. Before the measurement small fiber samples were cut under liquid nitrogen. The pieces were attached to a sample

holder with conductive double-sided carbon tape. The samples were subsequently sputter-coated with an 8 nm gold layer by a Cressington 108 auto sputter coater.

Determination of the diameter for the tensile tests: The fibers were cut into pieces about 5 cm in length for the tensile test. On both sides of the fiber, 3-5 fiber pieces (with a length of approx. 2 mm) were cut for SEM specimens and a cross-section image was taken for each fiber as described before. The cross-sectional images were used to determine the surface area A with the software ImageJ. From the area, the diameter d was calculated using the formula for a circle diameter ($A = d^2 \pi/4$). Afterward, the mean value was calculated from the obtained 5-10 diameter values and used for the tensile tests.

Single fiber tensile strength: Tensile tests were performed using a tensile tester (zwickiLine Z0.5, BT1-FR0.5TN.D14, Zwick/Roell, Germany) with a clamping length of 10 mm, a crosshead rate of 5 mm/min at 25°C and a pre-tension of 0.001 N. The load cell was a Zwick/Roell KAF TC with a nominal load of 20 N. The single fibers were glued to a paper frame according to standard DIN1007 for single fibers tensile strength measurements (test length 25 mm). The fiber tensile tests were performed by a fiber test program and the input parameter was the average diameter which was determined by SEM for each fiber individually. After the tensile test measurement, quantitative analysis of the tensile strength and Young's modulus was carried out by Origin 2022 software.

Thermogravimetric analysis: Thermogravimetric measurements were performed by a simultaneous TGA/DSC device (STA449 F5 Jupiter system, Netzsch, Germany). Therefore 5-20 mg samples were measured in an Al₂O₃ crucible. The heating curve was set to 5 K min⁻¹ in air respectively nitrogen and the samples were heated to the required temperature.

Attenuated total reflectance fourier transform infrared spectroscopy: ATR FT-IR studies were performed on a Tensor 27 system (Bruker, Germany) equipped with an ATR unit with a diamond crystal. After a background measurement, the samples were ground to a fine powder with a mortar and pressed against the measuring diamond to receive a sufficient signal. The measurements took place in a wavenumber range of 4000-400 cm⁻¹ at a resolution of 5 cm⁻¹. The mean of 32 measurements per sample was calculated to obtain

higher signal-to-noise ratios. After the measurement, a baseline correction by the ATR FT-IR software (OPUS) was performed, and the measured data were saved as a .CSV file and plotted graphically using the Origin software.

Raman: A combined Raman-imaging / scanning force microscope system (WITTEC ALPHA 300 RA+, Germany) with WiTec Control FIVE 5.3 software was used for Raman measurements. The laser was equipped with a UHTS 300 spectrometer combined with a back-illuminated Andor Newton 970 EMCCD camera (Resolution: ca. 300 - 400 nm (lateral) and 900 nm (z) with 100x objective).

The measurements were carried out at an excitation wavelength of $\lambda = 532$ nm and a laser power of 1 mW with 50 accumulations with an integration time of 0.5 s pixel⁻¹. The samples were stacked on a glass slide. After adjusting the focus on the fibers at 100x magnification, the Raman spectrum was recorded. A cosmic ray removal and a baseline correction were performed on all spectra.

Nuclear magnetic resonance: NMR experiments were performed with a Bruker Avance II 300 (magnetic field 7.05 T) spectrometer in a 4 mm triple resonance sample head (also from Bruker) at a rotation speed of 10 kHz.

The ²⁹Si MAS NMR measurements were performed using a single-pulse quantitative experiment with a 90° pulse length of 3.5 μ s, a recycle delay of 60 s, and no proton decoupling during acquisition. The spectra were indirectly referenced with $N(\text{SiMe}_3)_3 / \sigma(\text{iso}) = 2.4$ ppm, with respect to tetramethylsilanes (TMS) ($\sigma(\text{iso}) = 0.0$ ppm).

Small angle X-ray scattering (SAXS): Scattering patterns were recorded with the SAXS system "Ganesha-Air" from (SAXSLAB, Xenocs). The X-ray source of this laboratory-based system was a D2-MetalJet (Excillum) with a liquid-metal anode operating at 70 kV and 3.57 mA with Ga-K α radiation ($\lambda = 0.1341$ nm) providing a very brilliant and a very small beam (<100 μ m). The beam was focused with a focal length of 55cm using a specially made X-ray optic (Xenocs) to provide a very small and intense beam at the sample position. The different fibers were placed in small bundles to give enough scattering volume in the vertical direction with respect to the X-ray beam. We used an EIGER2-4M (Dectris) at a distance of 16cm as the detector. The circularly averaged data were normalized to the incident beam, counts per

solid angle, and measurement time before subtraction of the background measurement (air). From these curves, the appropriate q range for the azimuthal plots was deduced for the azimuthal averaging ($15\text{-}20\text{ nm}^{-1}$). Also for the azimuthally averaged data air was used as the background. The azimuthal peaks from the graphite crystals were fit in Origin with a simple Gauss function to get the FWHM and calculate the order parameter as was done previously.⁴³ To get the crystallite sizes the peaks from the radially averaged data were fit also with a Gaussian and the Scherrer equation was used to receive an approximate crystal size and compare the different fibers in this aspect. The individual values from the fits can be found in **Table S2** and **Figure S1**.

Transmission electron microscopy (TEM): TEM measurements were performed by a JEM-2200FS TEM (JEOL Corporation, Japan) at an acceleration voltage of 200 kV. For the sample preparation, the fibers were ground into particles and dispersed in ethanol (99.8 %, Sigma-Aldrich Co.) in an ultrasonic bath. A small droplet of the suspension was put onto the copper grid and the sample was dried on a paper filter for one day.

Elemental analysis: Measurements were carried out at Mikroanalytisches Labor Pascher (www.mikrolabor.com, Germany). According to the company, the following methods were used:

Carbon in the polymer, oxidized, and ceramic state

The samples were burned with a combustion additive at about $1200\text{ }^{\circ}\text{C}$ in a stream of oxygen; the contained carbon burned to CO_2 . The CO_2 was dissolved in a sodium hydroxide solution and the carbon content in the sample was calculated from the change in electrical conductivity (conductometry).

Hydrogen in the polymer, oxidized, and ceramic state

The samples were burned at $1050\text{ }^{\circ}\text{C}$ in an oxygen stream. The combustion water formed was determined by IR spectroscopy.

Nitrogen in the polymer and oxidized state

The sample was melted at a temperature of $900\text{ }^{\circ}\text{C}$ in the oxygen stream with a catalyst. Ammonia, N_2 , or NO_x formed was passed over copper oxide and reduced to N_2 after switching the carrier gas to CO_2 , excess oxygen was bound. The nitrogen formed was purged into an

azotometer. Acidic reaction gases and the carrier gas CO₂ were bound by potassium hydroxide solution. The nitrogen gas was measured volumetrically.

Nitrogen in the ceramic state

The sample was degassed in a heated graphite crucible. The released nitrogen was measured with helium as the carrier gas with thermal conductivity detection.

Oxygen in the polymer and oxidized state

Samples were pyrolyzed at 1500°C in a glass carbon tube with carbon contact. Oxygen was detected as CO and measured by thermal conductivity detection.

Oxygen in the ceramic state

The sample was degassed in a hot graphite crucible. The CO/CO₂ produced by the reaction of the released oxygen with the graphite was pumped off and detected by IR spectroscopy.

Silicon in the polymer and oxidized state

After pressure digestion with nitric acid, the silicon dioxide formed was digested with sodium hydroxide solution under pressure. Detection was carried out by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy).

Silicon in the ceramic state

The sample was digested under melting (with a soda-borax mixture in a Pt crucible) and then dissolved with water. The silicon analysis was carried out by ICP-AES.

Burning experiments: For the burning experiments, 40 carbon and C/SiCON-40 fibers were combined into a bundle. The fibers were attached to a self-constructed metal frame using aluminum tape. On the opposite side, a piece of paper was applied using superglue and loaded with two magnets weighing 30 g in total. The fibers were then burned in the center using a gas flame and the time taken for the fibers to break was measured. A temperature sensor was used to ensure that the fibers were always in the 1200 °C range of the flame. The whole burning process was recorded on video.

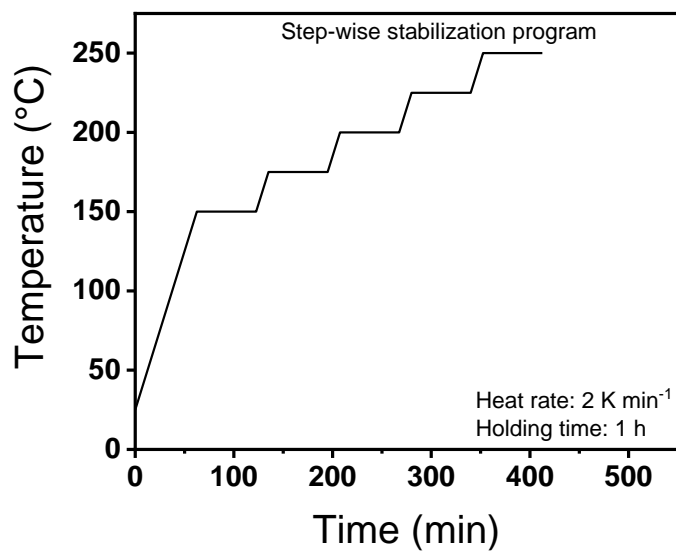


Figure S1. Step-wise stabilization program in air. With heating a heating rate of 2 K min⁻¹ and holding times of 1 h every 20 °C, starting at 130 °C.

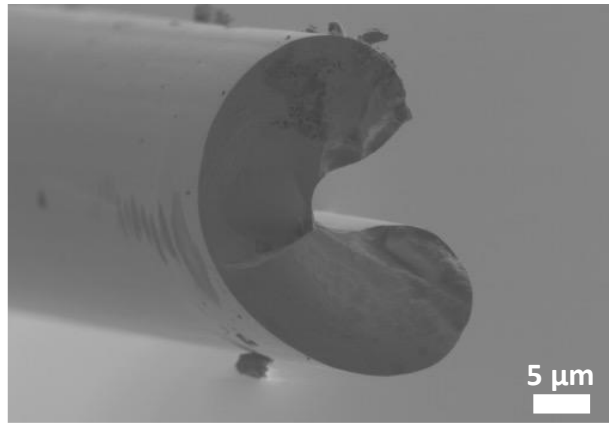


Figure S2. SEM image of the cross-section of C/SiCNO-40 fiber derived from the PAN/OSZ-40 precursor fiber produced in pure toluene.

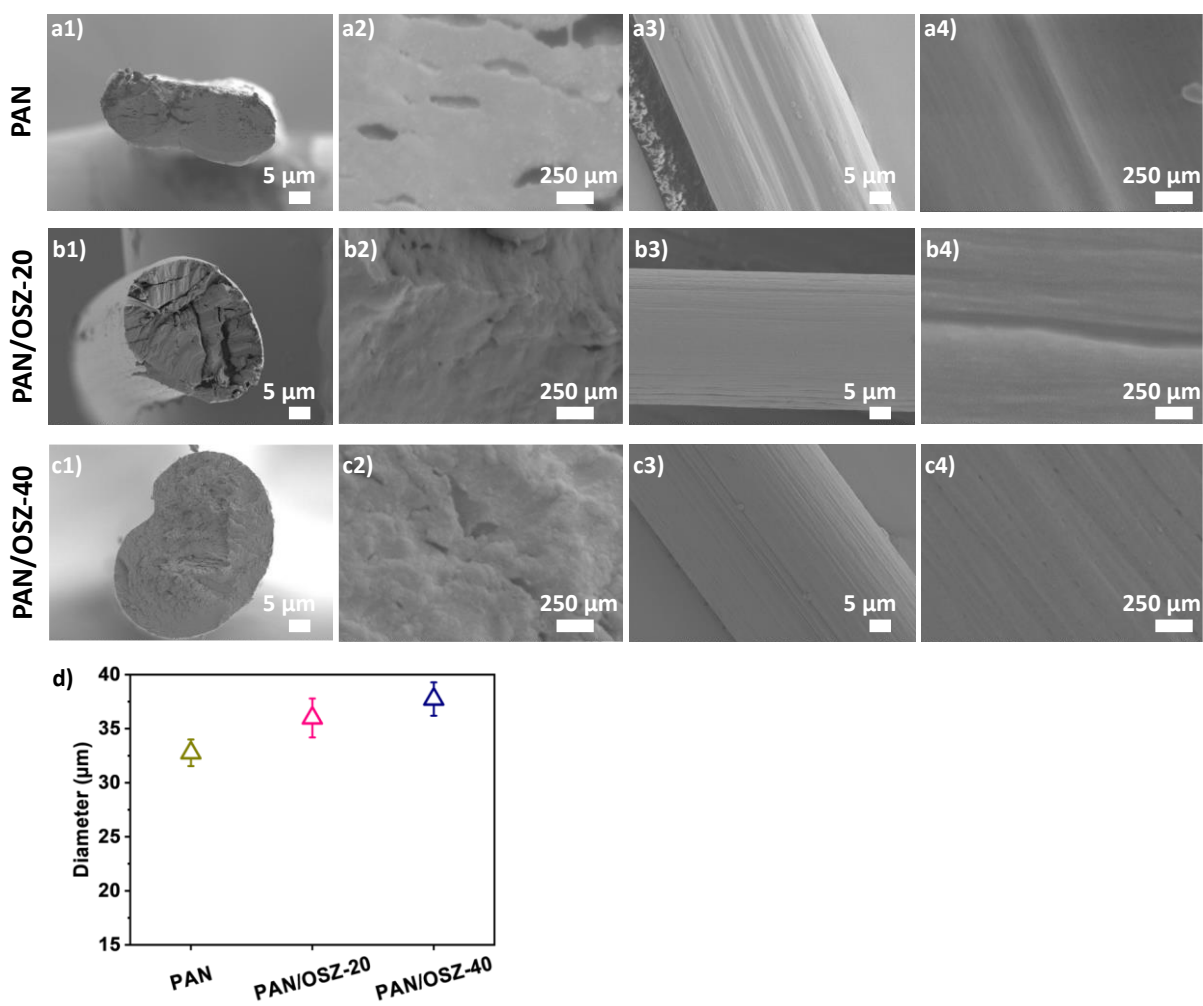


Figure S3. (a-c) SEM images in the cross-section and the longitudinal direction of PAN (a), PAN/OSZ-20 (b), and PAN/OSZ-40 (c) fibers. (d) Diameter of fibers with different amounts of OSZ.

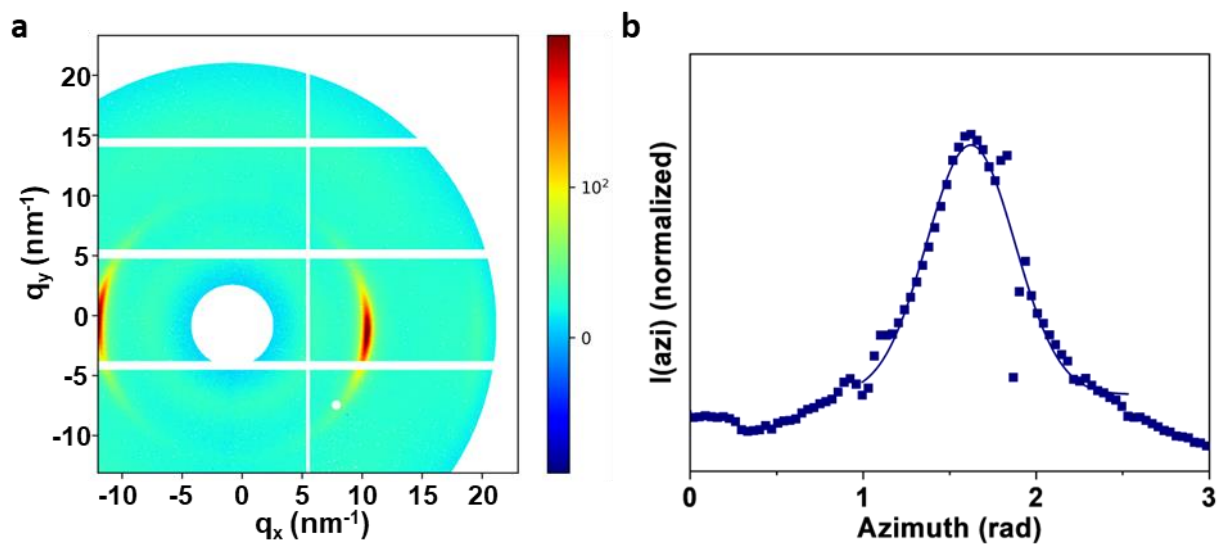


Figure S4. (a) 2D WAXS patterns of PAN/OSZ-40 composite fibers. (b) The azimuthal scan profiles of 2D WAXS patterns in panel (a).

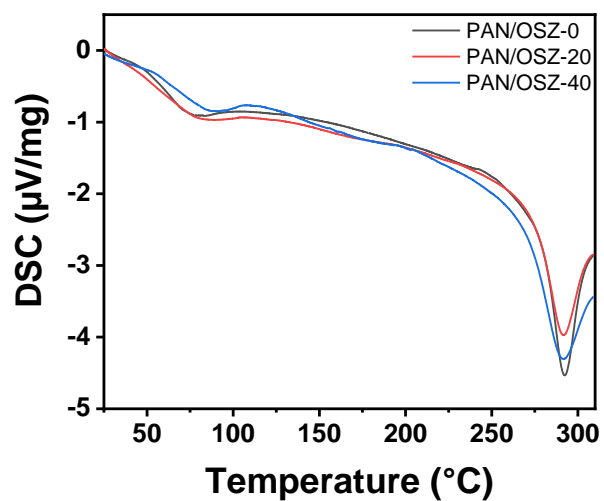


Figure S5. Differential scanning calorimetry of 0, 20, 40 wt.% PAN/OSZ fibers during the stabilization process (heating rate 5 K min⁻¹, atmosphere: air).

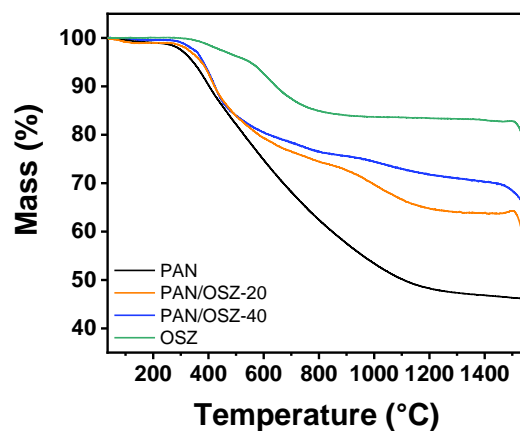


Figure S6. Thermogravimetric analysis of stabilized PAN fibers, PAN/OSZ fibers with different contents of OSZ, and pure OSZ (heating rate 5 K min⁻¹, atmosphere: N₂).

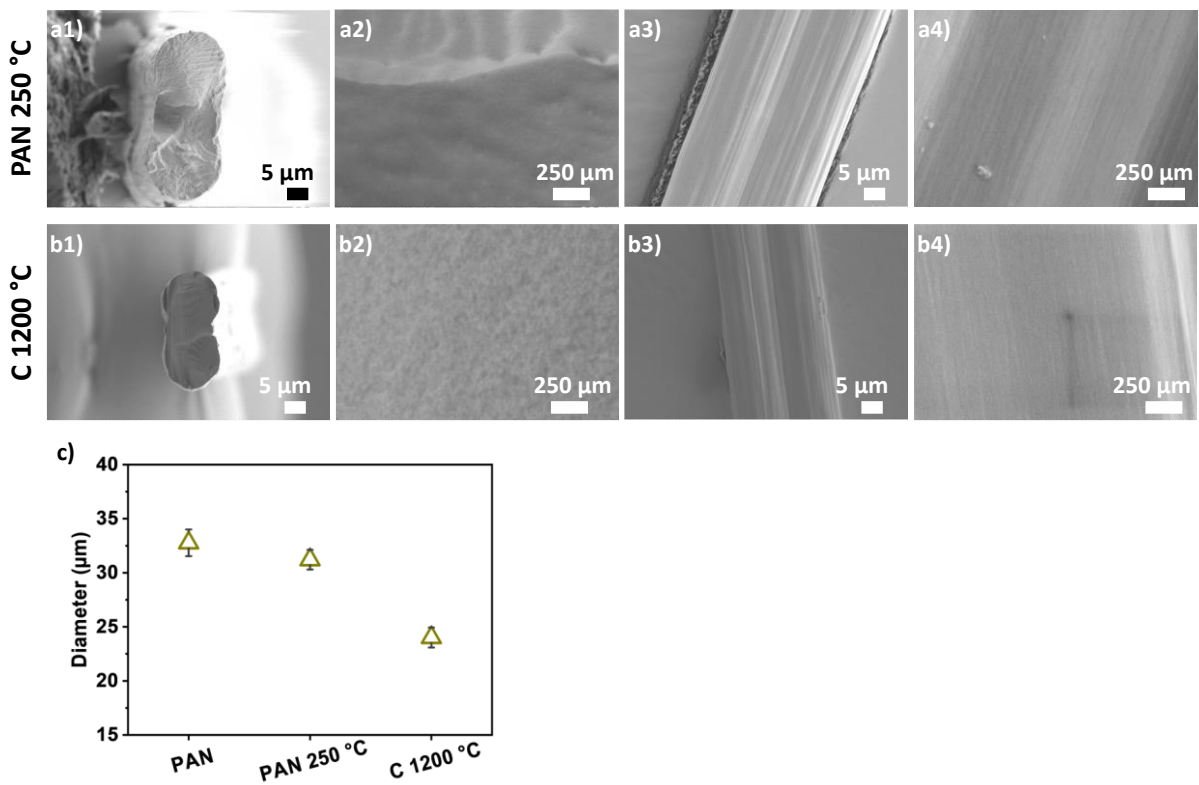


Figure S7. (a and b) SEM images in the cross-section and the longitudinal direction of stabilized PAN fibers at 250 °C (a) and the pyrolyzed carbon fibers at 1200 °C (b). (c) Diameter of fibers during polymer, stabilized, and pyrolyzed statuses.

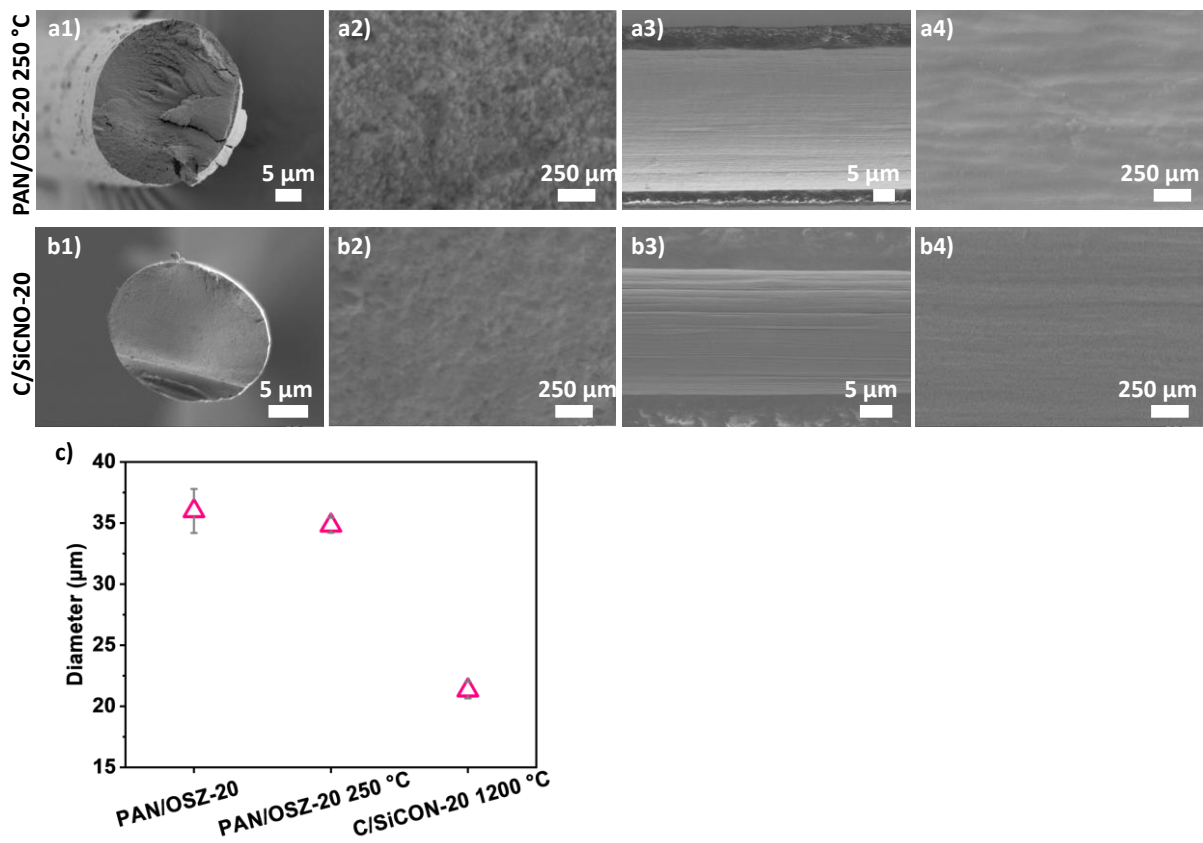


Figure S8. (a and b) SEM images in the cross-section and the longitudinal direction of stabilized PAN/OSZ-20 fibers at 250 °C (a) and the pyrolyzed C/SiCON-20 fibers at 1200 °C (b). (c) Diameter of fibers during polymer, stabilized, and pyrolyzed statuses.

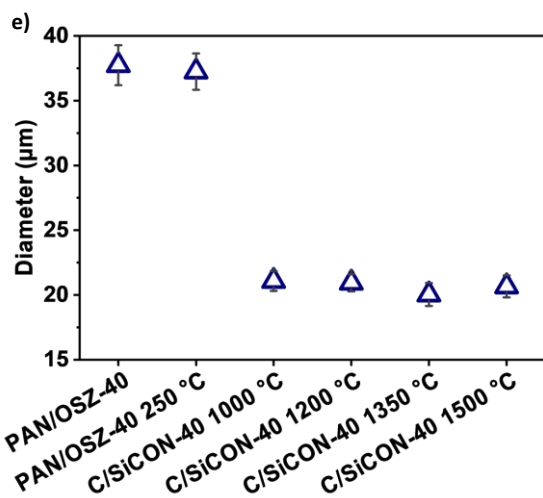
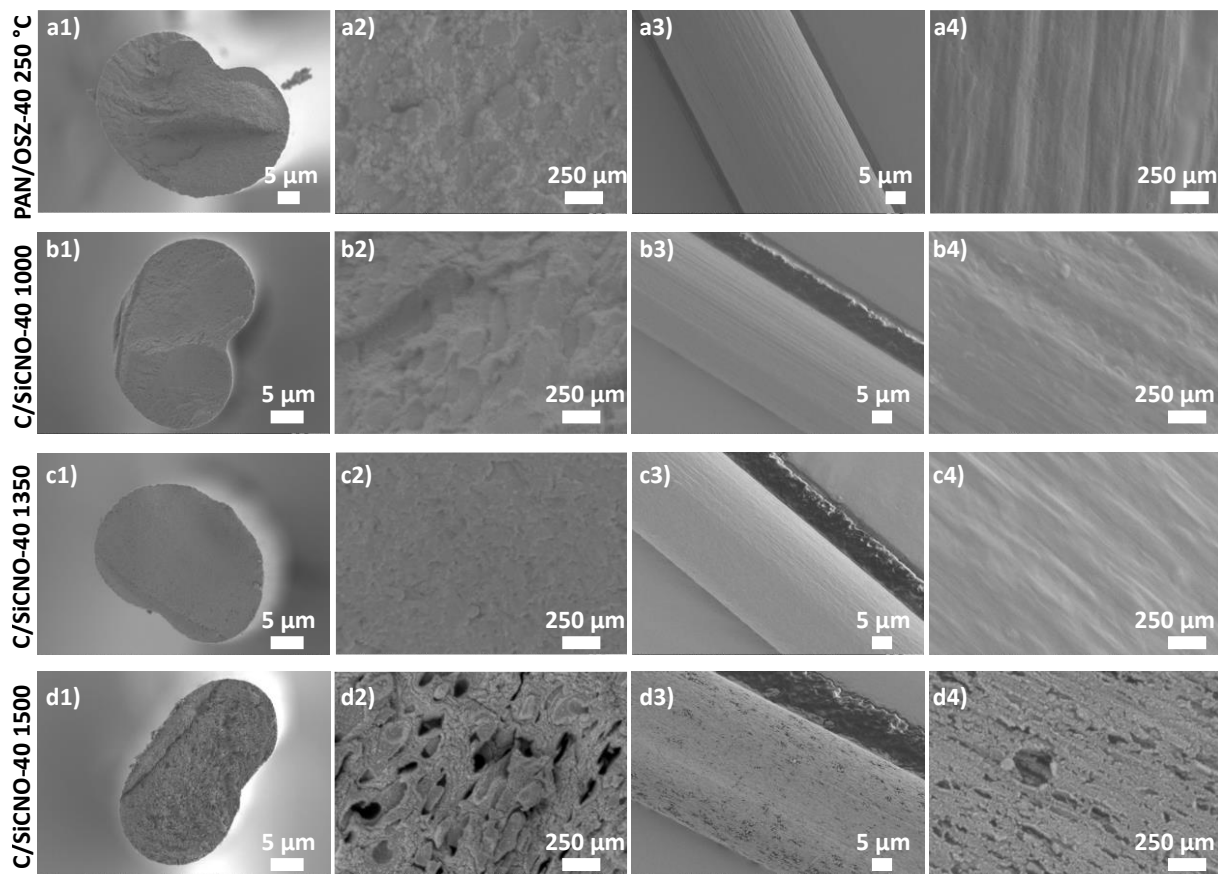


Figure S9. (a-d) SEM images in the cross-section and the longitudinal direction of stabilized PAN/OSZ-20 fibers at 250 °C (a) and the pyrolyzed C/SiCON-20 fibers at 1000 °C (b), 1350 °C (c), 1500 °C (d), respectively. (e) Diameter of fibers during polymer, stabilized, and pyrolyzed statuses.

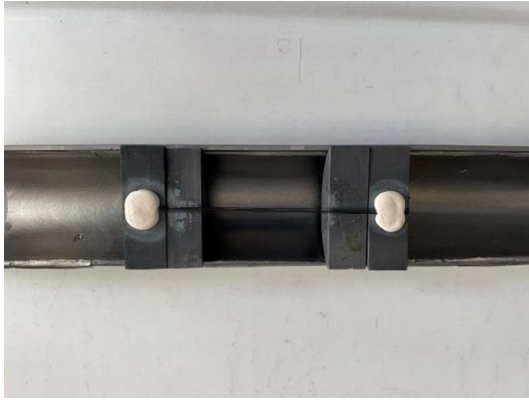


Figure S10. Setup and attaching of fiber rovings with a length of 5-8 cm with mullite glue on carbon pieces inside quartz glass crucibles. Left: oxidize PAN/OSZ-40 fibers before pyrolysis; right: pyrolyzed C/SiCON-40 fibers.

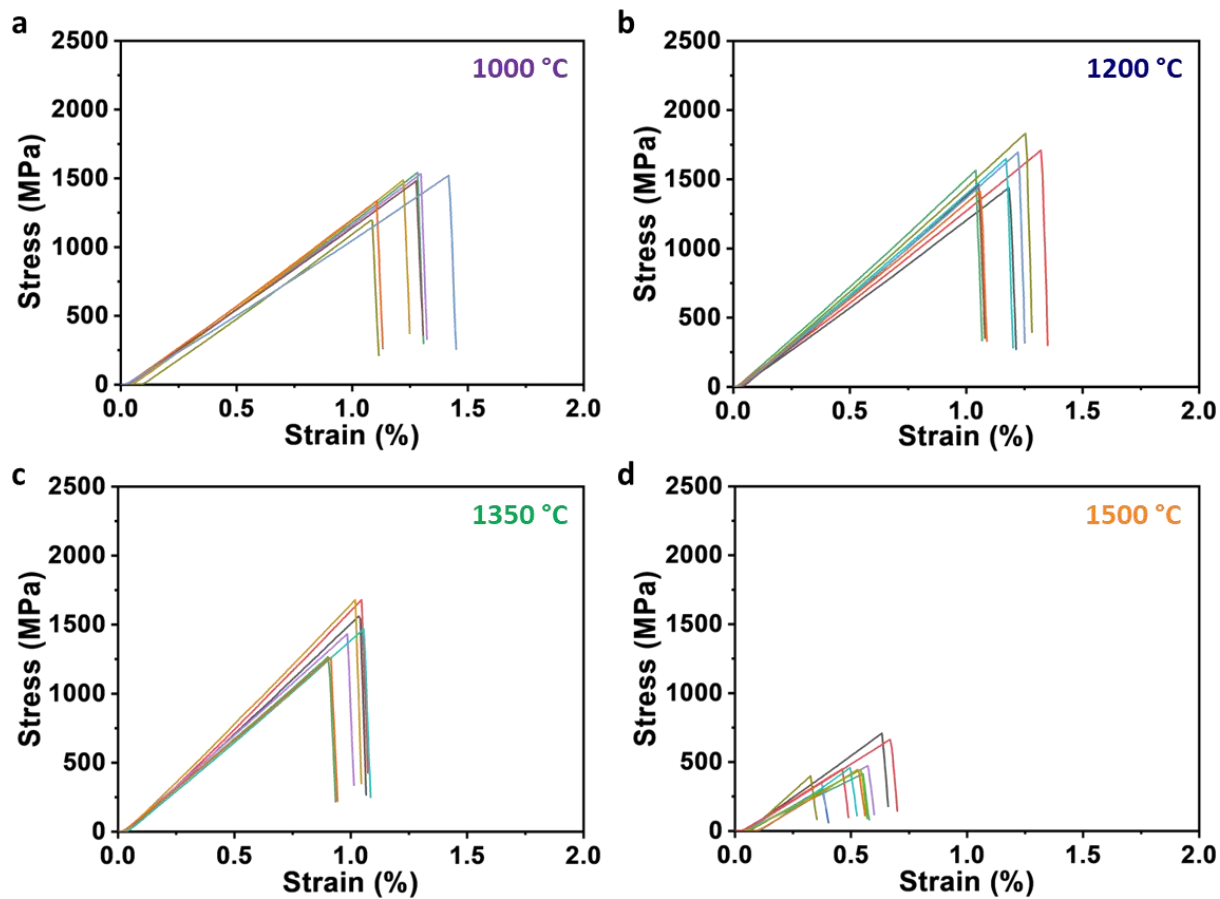


Figure S11. Stress-stain curves of noncontinuous C/SiCON-40 composite fibers pyrolyzed at different temperatures: (a) 1000 °C, (b) 1200 °C; (c) 1350 °C; (d) 1500 °C.

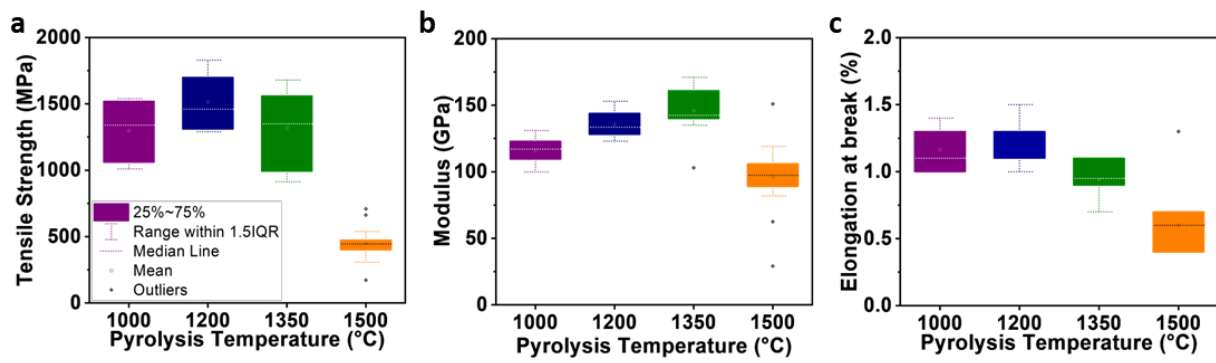


Figure S12. Comparisons of the mechanical properties of noncontinuous C/SiCON-40 composite fibers pyrolyzed at different pyrolysis temperatures: (a) tensile strength; (b) Young's modulus; (c) elongation at break.

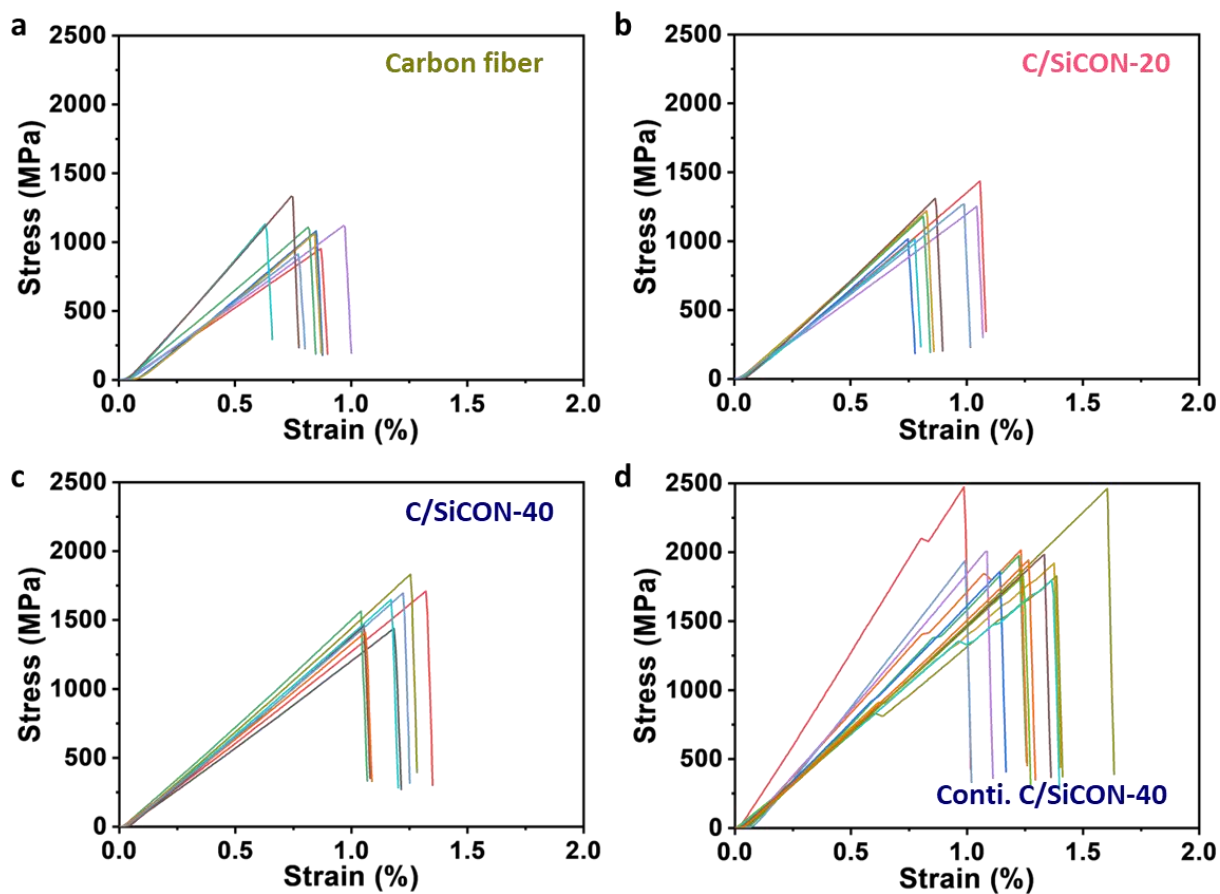


Figure S13. Stress-stain curves of fibers pyrolyzed at 1200 °C: (a) noncontinuous carbon fibers; (b) noncontinuous C/SiCON-20 fibers; (c) noncontinuous C/SiCON-40 fibers; (d) continuous C/SiCON-40 fibers.

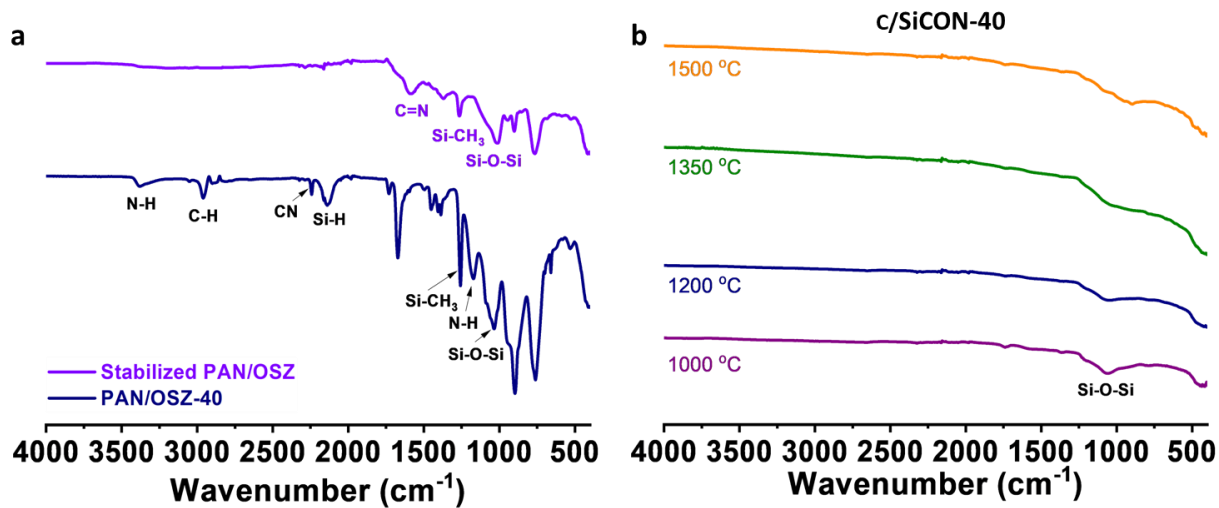


Figure S14. (a) ATR-FTIR spectra of the polymer (dark blue line), stabilized (purple line). (b) ATR-FTIR spectra of the carbonized/ceramicized fibers from PAN with 40 wt.% OSZ.

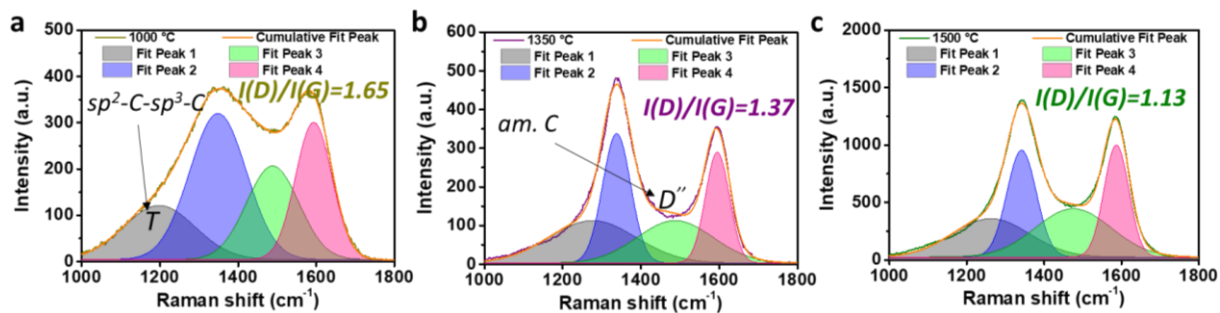


Figure S15. Curves fitted in Raman spectra of C/SiCON-40 composite fibers pyrolysis at different temperatures with a Gaussian function: (a) 1000 °C; (b) 1350 °C; (c) 1500 °C. The ratio of $I(D)$ to $I(G)$ exhibits a negative correlation with temperature, with decreasing values observed at higher temperatures.

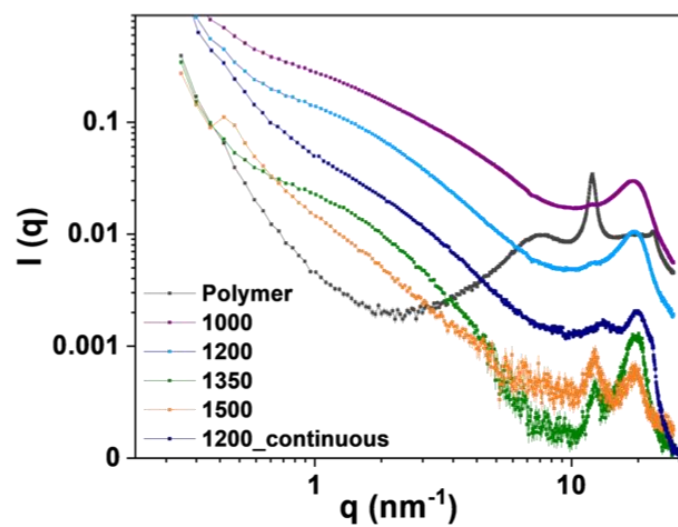


Figure S16. Small-angle X-ray scattering (SAXS) profiles of PAN/OSZ-40 precursor fiber, noncontinuous C/SiCON-40 fibers pyrolyzed at different temperatures, and continuous C/SiCON-40 fibers pyrolyzed at 1200 °C.

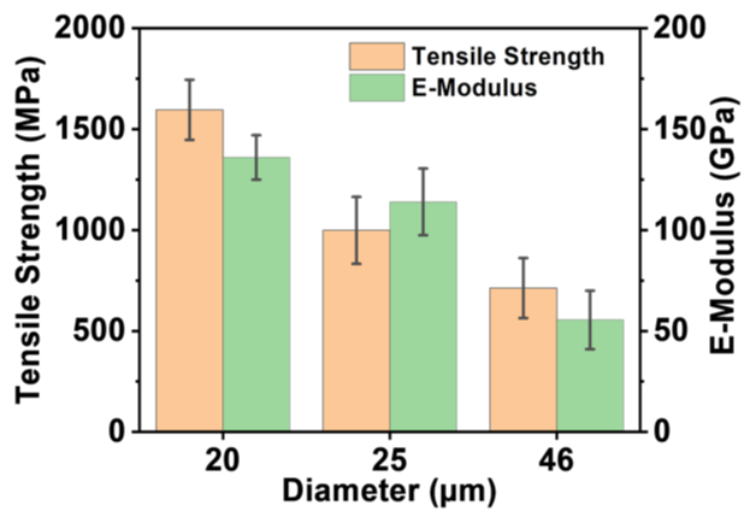


Figure S17. Changes in mechanical properties of C/SiCON-40 fiber with different diameters of fiber.

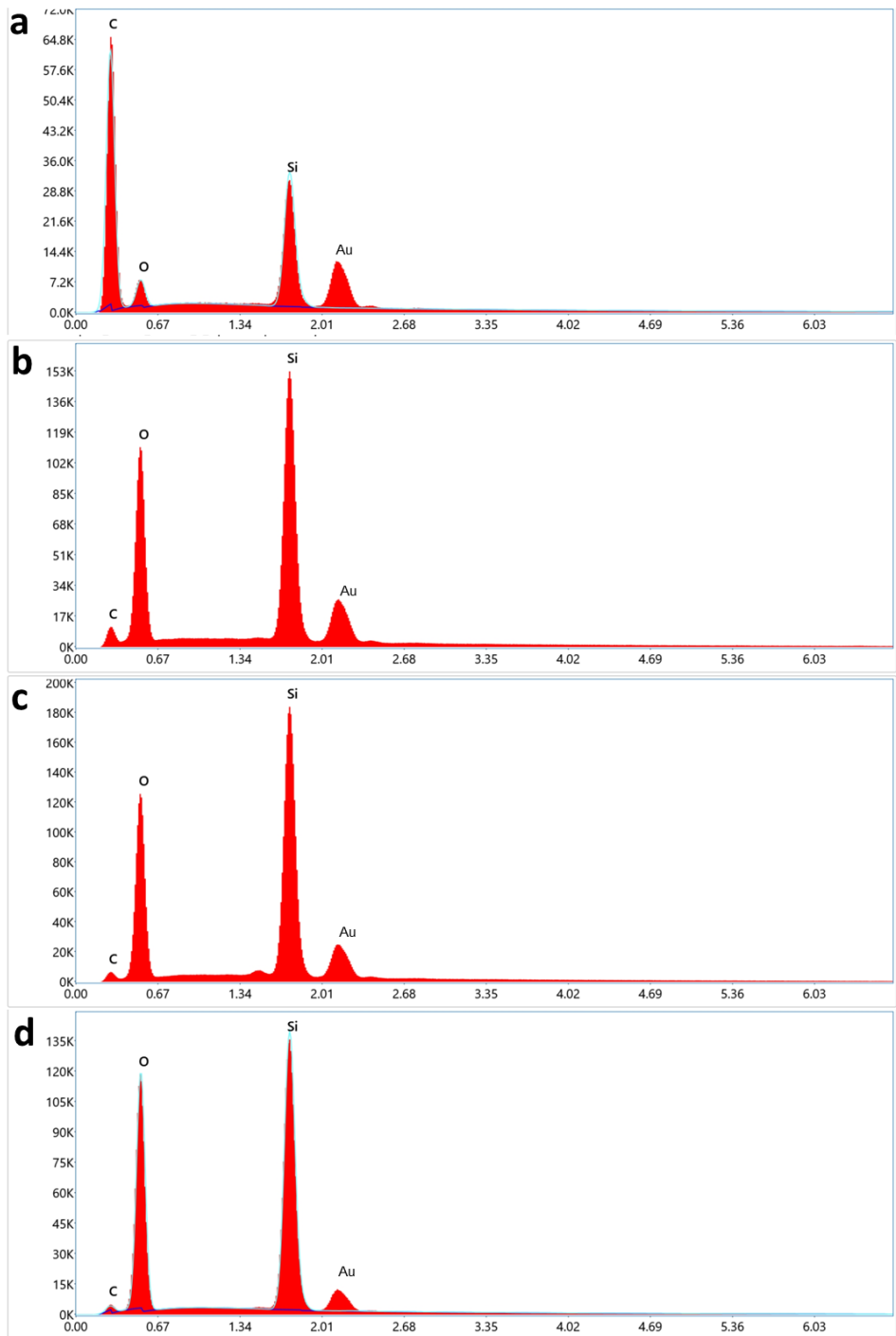


Figure S18. Changes in the elemental composition of C/SiCON-40 hybrid fibers in SEM-EDS analysis under thermomechanical loading at 1200 °C in air. (a) for 0 seconds (before treatment); (b) for 4 seconds; (c) for 30 seconds; (d) for 2 minutes.

Table S1: Compositions and parameters of wet spinning solutions of PAN/OSZ-0 to 40 fibers.
3 wt.% DCP was added to OSZ.

Content (wt.%)	PAN (g)	OSZ (g)	DMF (g)	DMF in bath (vol%)	SR
0	3	-	15.0	20	9
20	3	0.75	15.0	20	6
40	3	2.0	16,7	30	5

Table S2: Crystal orientation factor and crystallite size of the PAN/OSZ-40 precursor fiber, noncontinuous C/SiCON-40 fibers pyrolyzed at different temperatures, and continuous C/SiCON-40 fibers pyrolyzed at 1200 °C.

Sample	Crystal orientation factor	Crystallite size [nm]
PAN/OSZ-40 ^a	0.80	6.6
C/SiCON-40 1000	0.73	0.97
C/SiCON-40 1200	0.75	1.58
C/SiCON-40 1350	0.75	1.9
C/SiCON-40 1500	0.72	2.46
Cont. C/SiCON-40 1200	0.76	2.51

^a For PAN the peak at $q=12.1 \text{ nm}^{-1}$ was used

Table S3: Elemental composition calculated and measured for the polymer, stabilized state and measured after pyrolysis at 1200 °C (measurements done by Pascher www.mikrolabor.com).

Sample	Composition (at.%)					Empirical formula normalized on silicon
	C	H	O	N	Si	
Polymer	31.7	47.5	6.6	10.2	3.9	SiC _{9.06} H _{12.06} N _{2.59} O _{1.68}
Stabilized	31.9	43.6	11.0	9.1	4.5	SiC _{7.07} H _{0.23} N _{2.02} O _{2.43}
1200 °C	62.9	2.4	16.9	7.6	10.2	SiC _{6.14} H _{0.23} N _{0.75} O _{1.64}

Table S4: Comparisons of mechanical properties and diameter of our fibers with commercial fibers.

Fibers	Tensile Strength [GPa]	Young's modulus [MPa]	Diameter [μm]	Reference
C-fiber	1.1	140	20.0	This work
C/SiCON-20	1.2	140	21.3	This work
C/SiCON-40	1.5	136	20.9	This work
Conti-C/SiCON-40	2.0	175	20.0	This work
T300 (carbon)	3.5	230	7	2
T1100 (carbon)	7.0	320	5	2
M60J (carbon)	3.8	588	5	2
Nicalon 200N (SiC 1 st gen.)	3.0	210	14	3
Hi-Nicalon (SiC 2 nd gen.)	2.8	270	12	3
Sylramic (SiC 3 rd gen.)	3.2	~400	10	3

Notes and references

1. X. Liao, M. Dulle, J. M. de Souza e Silva, R. B. Wehrspohn, S. Agarwal, S. Förster, H. Hou, P. Smith and A. Greiner, *Science*, 2019, **366**, 1376-1379.
2. TORAYCA™ Technical Manual, Toray Composite Materials America, Inc., <https://www.toraycma.com/products/carbon-fiber/>.
3. O. Flores, R. K. Bordia, D. Nestler, W. Krenkel and G. Motz, *Adv. Eng. Mater.*, 2014, 16, 621-636.