Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information

SCIP: A New Simultaneous Vapor Phase Coating and Infiltration Process for Tougher and UV-resistant Polymer Fibers

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Sample preparation

Sample for mechanical testing

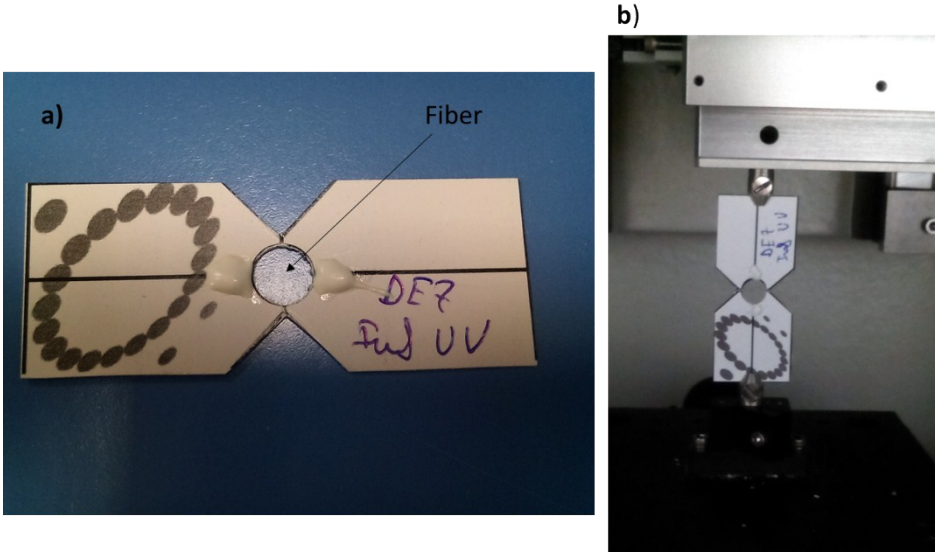

Fig.S1: For the measurement of the modulus of toughness of the samples tensile tests were performed on individual fibers. a) The fibers were aligned on a cardboard jig that was b) subsequently clamped to the mechanical tester from both sides. Uniaxial force was applied and the displacement measured in the fiber´s direction until its failure.

Sample for ATR-FTIR

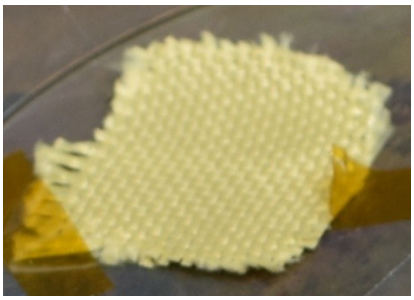

Fig.S2: 1x1 cm cut of Kevlar29 fiber cloth. This fabric is appromimately 0.3 mm thick

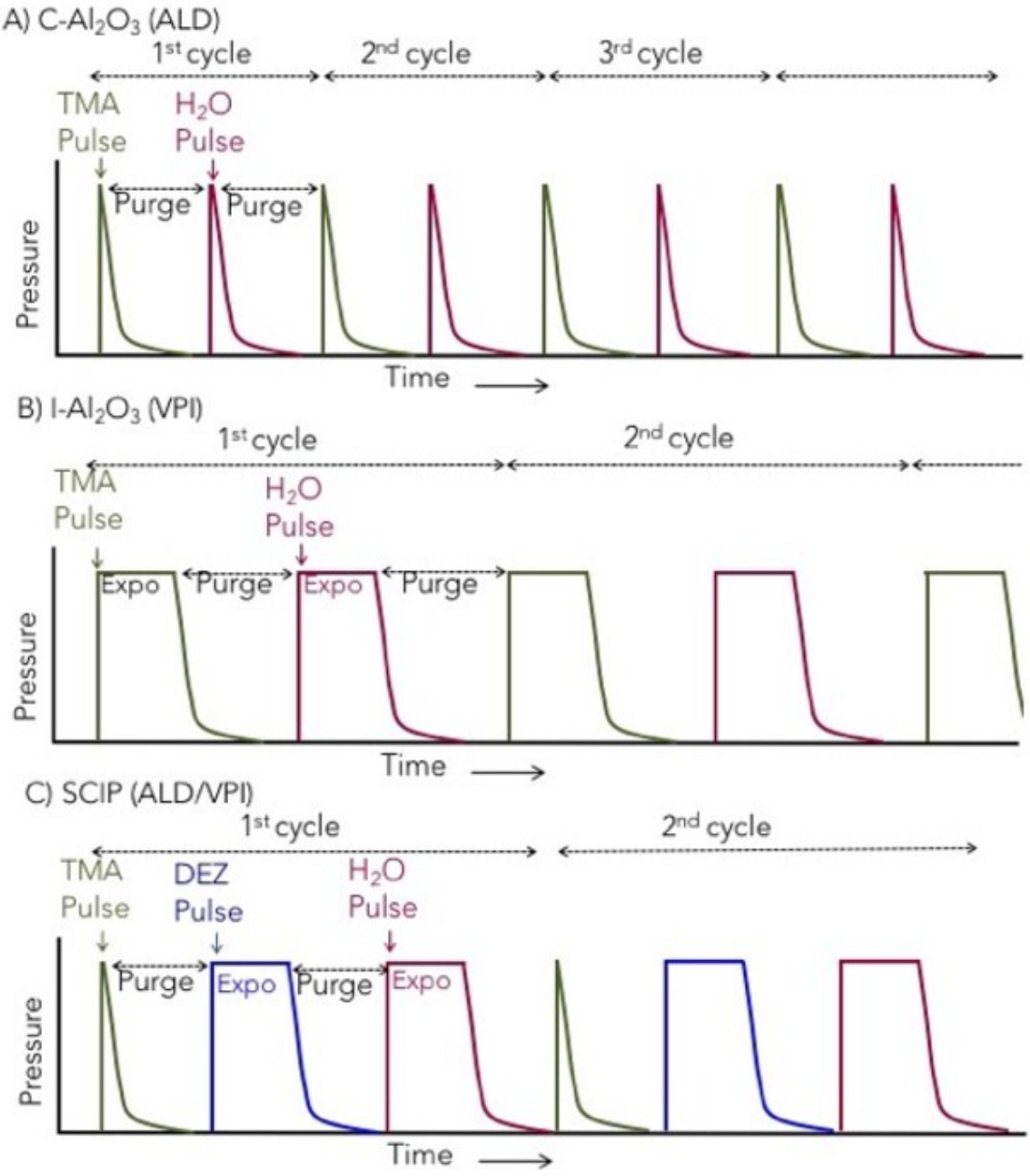

Fig.S3: Process scheme of SCIP and SEM images of the different samples. Schematic of the pressure profile of the different sample preparation processes for A) ALD (C-Al2O3), B) VPI (I-Al2O3), and C) SCIP.

Table S1: **Results of the Weibull analysis for all the analyzed fibers.**

Sample	m	Characteristic modulus (MPa)	Experimental modulus (MPa)	%Difference
Kevlar	13,6	95,2	92,3	3,1
Kevlar UV	18,7	42,2	41,3	2,2
I-Al_2O_3	15,3	100,7	98,3	2,5
I-Al_2O_3 UV	3,0	80,3	55,1-83,4	27,2
C-Al_2O_3	10,5	110,4	105,45	4,7
C-Al_2O_3 UV	7,8	66,4	59,3-79,8	6,9
SCIP	14,1	111,5	107,4	3,8
SCIP UV	13,0	104,5	107,3	2,7

Compared to the values reported in the literature for high performance fibers, [1] most of the analyzed fibers show a relatively high Weibull modulus (m) (from 10 to 18), indicating only a little variation from sample to sample. The high reliability is also reflected in the small difference between the calculated characteristic MOT and the experimental values (in most of the cases below 5%).
However, the UV irradiated C-Al_2O_3 and I-Al_2O_3 fibers showed a very low Weibull modulus (< 8) and a large difference between the calculated and experimental values (above 5%). Therefore, the MOT of the I-Al_2O_3 and C-Al_2O_3 fibers after UV irradiation must not be considered as a single value but it might be best represented as a range of values.

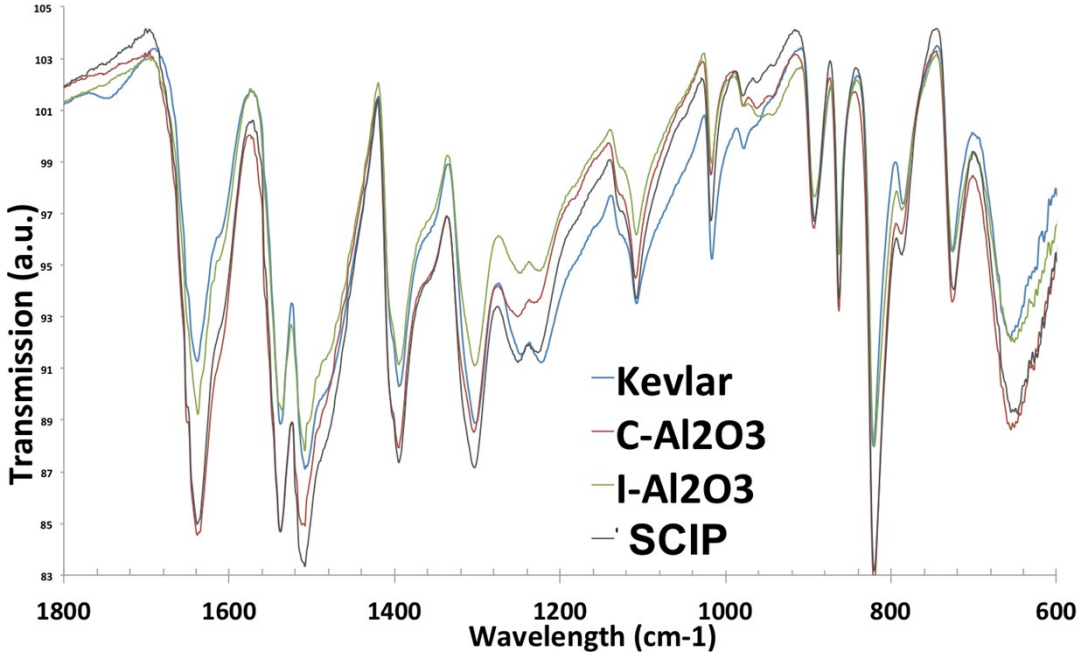

Figure S4: Fingerprint area of the ATR-FTIR spectra of the samples showing the biggest differences in the area between 900 and 1000 cm^{-1}

The chemical changes in the FTIR spectra shown in Figure S4 and Table S2 are given by a sum of contribution of both the infiltrated subsurface of the fiber and the untreated bulk and have been recorded by using attenuated total reflection (ATR)- FTIR.
Compared with FTIR in transmission, ATR-FTIR offers several advantages, among those the possibility to measure Kevlar29 fibers and cloth (Fig.2 supporting info) as they are, i.e. without any sample preparation. Note that Kevlar fibers are only soluble in hot concentrated H_2SO_4 and therefore a solution for FTIR can´t easily be prepared. ATR-FTIR also permits to contact the ALD treated woven directly with the ATR crystal, in this way ensuring that the obtained spectrum emphasizes the contribution of the infiltrated subsurface over the untreated bulk, since the depth of penetration of the evanescent wave is limited and strongly decays with penetration depth. The sensitivity of this technique is very high. ATR is capable of detecting molecules present in concentrations down to 0.1% [5]

Table S2: Position of the amide-related peaks in FTIR spectra (in cm^{-1})

	Kevlar	C-Al_2O_3	I-Al_2O_3	SCIP
N-H st	3310	3310	3308	3306
Amide I	1641	1642	1638	1639
Amide II	1539	1538	1540	1538
Amide III	1249 1222	1251 1221	1250 1224	1251 1227

Table S3: **Relative change of the intensities of the amide peaks after UV irradiation**

	Intensity change (%)			
	N-H st	Amide I	Amide II	Amide III
Kevlar	-7	2	2	-3
C-Al_2O_3	-4	3	1	-3
I-Al_2O_3	-5	0	-1	-4
SCIP	-1	0	1	0

The UV light has the strongest impact on untreated Kevlar. The reduction of the intensity of the N-H stretching and Amide III bands, together with the increased intensity of the Amide I and II bands, indicate cleavage of H-bonds between adjacent chains and a homolytic splitting of C-N and N-H bonds. [2-4] The degradation is to some extent suppressed upon coating or infiltration with Al_2O_3. The I-Al_2O_3 samples are less sensitive to UV light than native Kevlar, likely due to parallel occurrence of chain scission and cross-linking of the polymer. However, the cross-linking does not completely compensate the effect of the chain-scission upon exposure to UV light. In the C-Al_2O_3 samples, the polymer did not undergo serious alteration and the metal oxide absorbs the UV light. However, a 25 nm thick alumina film on top of the fibers is not enough to completely screen the UV radiation. Thus, the C-Al_2O_3 and the I-Al_2O_3 samples show similar changes in the FTIR spectra after UV irradiation.

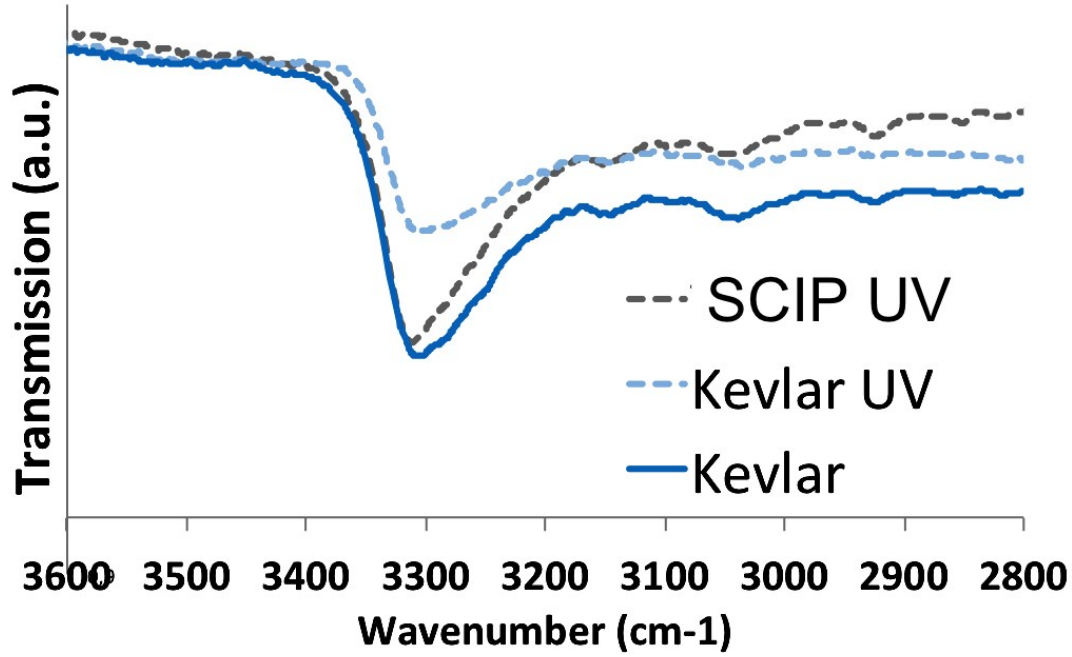

Figure S5: Intensity change on the example of the N-H vibration peak of Kevlar (blue), UV exposed untreated Kevlar (dashed light blue) and UV exposed TMA Pulse Kevlar (dashed grey), showing the biggest change occurring with untreated Kevlar after UV exposure. Prior to the intensity evaluation, all FTIR spectra have been normalized to the intensity of the peak for which no changes are expected (≈820 cm^{-1} corresponding to the vibration of the aromatic C-H bonds), individual sections selected, and baselines corrected with the software of the instrument. Finally, the resulting intensity values were compared.

References

(1) Naito, K. Tensile Properties and Weibull Modulus of Some High-performance Polymeric Fibers J. Appl. Polym. Sci. **2013**, 128, 1185–1192.

(2) Zhang, H.; Zhang, J.; Chen, J.; Hao, X.; Wang, S.; Feng, X.; Guo, Y. Effects of Solar UV Irradiation on the Tensile Properties and Structure of PPTA Fiber Polym. Degrad. Stab. **2006**, 91, 2761–2767.

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