# SUPPLEMENTARY INFORMATION

# Surface modification of aramid fibers - the key to chemically recyclable epoxy composites

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This supplementary information contains 19 Figures and 6 Tables on 22 pages.

#### Materials characterization

# Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

Secondary electron images were acquired with an ultrahigh resolution FE-SEM (Hitachi S4800). Microscope operating at an accelerating voltage of 5kV. All samples were Cr sputtered under vacuum (Cressington R208, UK) for 2 min (5 nm thick layer) to minimize charging effects. The spectroscopic characterization of the fiber mesh was performed by EDS analysis and mapping carried out at an accelerating voltage of 5 kV using the FE-SEM instrument, equipped with an X-Max 80mm<sup>2</sup> EDS detector from Oxford Instruments, UK.

# Atomic force microscopy (AFM)

Atomic force microscope (AFM), Nanoscope IIIa (Bruker AXS, Santa Barbara, CA) was used to investigate the surface topography, roughness, and average height of features on the surface of single filaments of aramid fibers. The fibers were carefully placed on an adhesive tape and the ends of the fibers were fixed with epoxy glue. The glue was allowed to dry at room temperature for 24 h before testing. The images were obtained with the aid of ScanAssyst. The surface roughness and average height values were obtained from acquired images of 5  $\mu$ m × 5  $\mu$ m size with the aid of the NanoScope® Analysis software using a 3<sup>rd</sup> degree plan fit followed by a 3<sup>rd</sup> degree flattening filter.

#### *X-ray photoelectron spectroscopy (XPS)*

Compositional analysis of the outermost surface (top 7-10 nm) of the meshes was conducted using a Kratos AXIS Supra X-ray photoelectron spectrometer using a monochromatic Al Ka source (15 mA, 15 kV) employing the charge neutralizer system. The meshes were mounted with the cut edges sealed using adhesive carbon tape, minimizing the exposed area in the UHV chamber. Elemental information and states of oxidation can be achieved for all elements, except for hydrogen and helium, with detection limits varying between 0.1-0.5 at.-%, depending on the specific element. Survey scans were acquired on two separate areas, sized  $300 \times 700 \mu$ m, on each fiber material using a pass energy of 160 eV. High resolution spectra were charge-corrected to the C 1s peak corresponding to adventitious carbon (C-C, C-H) set at 284.6 eV. The spectra were analyzed using the instrument software. Detailed deconvolution of the high-resolution spectra was made using Origin to fit the curves related to the C 1s, O 1s, N 1s

Analyzer" tool. As a second step, the curve was fitted by using the tool "Multiple Peak Fit", the peaks were selected and a Gaussian fit was applied until converge.

# Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy was performed with a PerkinElmer Spectrum 2000 spectrometer equipped with a single reflection-attenuated total reflectance (ATR) accessory using a DTGS detector with a polyethylene window. The accessory consists of a diamond crystal with an angle of incidence for the IR beam of 45 °. The spectra were acquired with 16 scans in a range between 600-4000 cm<sup>-1</sup> and with a 4 cm<sup>-1</sup> resolution. The spectra were obtained from two different points of the samples.

#### Thermal characterization

Differential scanning calorimetry (DSC) was carried out with a Mettler Toledo DSC 1 instrument. For the analysis 5–10 mg of sample was placed in aluminium crucibles. The cycle consisted of two heating and one cooling scans between –80 to 200 °C, under inert atmosphere established by N<sub>2</sub> flow of 50 mL/min and with a constant heating and cooling rate of 10 K min<sup>-1</sup>. The glass transition ( $T_g$ ) temperature was determined from the second heating scan as the midpoint of the transition. The  $T_g$  was determined as the average of three measurements. The thermogravimetric analysis (TGA) of all the samples was performed with a Mettler Toledo TGA/DSC 1 instrument. The analysis was carried out in alumina crucibles with approximately 5–10 mg of sample and under N<sub>2</sub> flow of 50 mL min<sup>-1</sup>. The temperature range was from 30 to 700 °C and a constant heating rate of 10 K min<sup>-1</sup> was applied. The DSC and TGA thermograms were processed with the aid of Mettler Toledo STARe v. 15.00 software.

# Nuclear magnetic resonance (NMR) spectroscopy

<sup>1</sup>H (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded with an Avance 400 spectrometer. The chemical shift ( $\delta$ ) of the residual DMSO (2.49 ppm) from DMSO-d6 was utilized as a reference.

### Size exclusion chromatography (SEC)

Performed on recycled resins by a SEC-curity 1260 system (Polymer Standards Services, Mainz, Germany) with two GRAM (Polymer Standards Services, Mainz, Germany) analytical columns 100 Å and 1000 Å in series. The system was coupled to a refractive index (RI) detector and photodiode detector. The eluent consisted of dimethylsulfoxide (DMSO, HPLC grade)

containing 0.5 wt% lithium bromide (LiBr). The flow rate of the eluent was set at 0.5 mL min<sup>-1</sup>. The standard calibration was performed using the data from an RI detector with PMMA standards. 5 mg of the recycled resin was dissolved in 1 mL of the eluent solution. The samples were filtered through a 0.45 μm polytetrafluoroethylene (PTFE) syringe filter prior injection.

#### Sample preparation for peeling test and lap-shear test

Samples for the peeling test were prepared with 10 cm x 10 cm virgin aramid meshes; v-UA, v-PDA and v-PDA-Si. The sample was placed in a mold and a sheet of Teflon with 3 cm width and 0.1 mm thickness was placed on one of the ends of the meshes to keep it as free end, thereafter the remaining part of the mesh was covered with pieces of pre-cured thermoset. Subsequently, the samples were post-cured in the hot press at 180 °C and 250 kN for 1 h. The samples were cut to a final dimension of 7 cm x 2 cm as exemplified in Fig. S2b.

Lap shear tests were utilized to assess the bonding characteristics between meshes and the thermoset matrix. The v-UA, v-PDA and v-PDA-Si meshes were tested in virgin state with virgin thermosets (TVx) and with recycled thermosets (TRx). In a second stage, the bonding characteristics of the meshes were tested after chemical recycling (r-UA, r-PDA and r-PDA-Si) with virgin thermoset (TVx). For that aim, a pre-cured piece of thermoset with a thickness of 1.3 cm and a width of 2 cm was placed on a free end of a mesh with average dimensions of 5 cm x 1.3 cm as exemplified in Fig. S2d. The thermoset was thereafter covered with another piece of mesh with the same dimensions. The specimens were post-cured at 180 °C and 250 kN for 1 hour.

### Single fiber and thermoset tensile test, peeling test and lap-shear tests

The mechanical testing was performed using a single column universal testing machine, Instron 5944. The mechanical properties of the fibers were evaluated by single fiber tensile tests with a load cell of 50 N. Specimens were prepared in accordance to the standard ASTM-C1557-20. The ends of single filaments with an effective gauge length of 25 mm were pasted with epoxy glue on a mounting tab as shown in Fig. S7d. The samples were left to dry for at least 24 h followed by conditioning at  $23 \pm 1$  °C and a relative humidity of 50% for 72 h prior to being tested. After fixing both of the ends of the card board in the grips, a cut in both the left and the right side of the card board was done, thereafter the specimens were tested with a cross head separation speed of 5 %/min.

The mechanical properties of the thermosets were evaluated using a 500 N load cell with a cross head separation rate of 100 %/min. At least 5 samples with a rectangular-shaped geometry (50 mm x 10 mm width and 1.3 mm thick) and effective gauge length of 20 mm were analyzed. The peeling test was performed using a 500 N load cell. At least two specimens of each sample: UA, PDA and PDA-Si, were tested. The free end of the polymer matrix and the free end of the aramid mesh were gripped with the upper and lower grip, respectively. The test was performed by pulling the free end of the polymer matrix from the mesh at a constant rate of 10 mm/min. The data was recorded until a 30 mm extension was reached. Lap shear bonding tests were performed on composites consisting of virgin meshes and virgin thermosets and corresponding composites with either recycled thermosets or recycled meshes. A 500 N load cell was utilized for pulling an end of the specimen at a constant rate of 100%/min until debonding.

# Self-polymerization of dopamine

The self-polymerization of dopamine has found applicability in a wide variety of fields from biomedical applications<sup>1–3</sup> to high-performing engineering devices.<sup>4</sup> This is mainly owed to the versatility of polydopamine as it has the ability to attach to materials with active surfaces, such as silica, but it can also activate inert surfaces such as aramid. This is because the self-polymerization and adhesion of polydopamine mainly relies on hydrogen bonding and  $\pi$ - $\pi$  interactions and therefore it does not require the presence of active functional groups.<sup>4–6</sup> Even when the precise mechanism for the self-polymerization and subsequent adhesion of polydopamine has not been elucidated, it is widely accepted that the first step consists of the oxidation of dopamine to yield dopamine quinone (Fig. S1), a molecule, which can be associated to the observed initial change of color of the solution from transparent to pinkish. The subsequent oxidation of this structure by dehydrogenation is expected to lead to a mixture of indole quinone monomeric units which thereafter form C-C bonds between them to form a variety of oligomeric structures of different sizes<sup>7–9</sup> (Fig. S1a). This intramolecular oxidative process can occur even in dopamine monomers that have been previously functionalized.<sup>2,3,9</sup>

In addition to the main proposed structures of polydopamine (Fig. S1c), some other species such as pyrrole carboxylic acid units (Fig. S1b) have also been reported. The formation of this carboxyl units in polydopamine has been explained by the oxidative process of indole quinone structures to carboxylic units, which can take place due to the *in situ* formation of  $H_2O_2$ .<sup>8</sup>

The structure of polydopamine contains a number of electrophilic and nucleophilic sites (Fig. S1c) which makes it suitable towards subsequent reactions, such as the condensation of silane coupling agents. This approach has already been successfully achieved by the group of Tian et al.<sup>10</sup> who obtained the best coating properties in a one pot approach with meta-phenylene terephtalamide fibers of 1 mm length.



Fig S1. a) Proposed routes for polydopamine formation and main monomeric units, b) reported monomer units with carboxylic moieties and c) main polydopamine structures reported in literature.



Fig. S2. Sample preparation scheme.

#### **XPS** analysis of aramid fibers

XPS analysis provided a deeper understanding of the surface chemistry by the evaluation of the deconvoluted curves of the C 1s, O 1s, N 1s and Si 2p spectra. The C 1s spectra of unmodified aramid (UA) is shown in Fig. 3a and it was fitted with three curves. The first curve presents a peak at 284.60 eV associated with C-C and C=C bonds. The second peak at 286.1 eV was assigned to the C-N bond while the peak at 288.5 eV can be ascribed to the carbonyl group of the aromatic amide.<sup>11</sup>

The N 1s spectra (Figure S3a) was fitted with two peaks, one at 400 eV corresponding to the nitrogen atom of the aromatic amide and one additional peak at 402.4 eV which could be due to impurities on the surface. The O 1s spectra (Fig. S3b) was fitted with two peaks as well, one at 532.1 eV ascribed to the oxygen atom of the aromatic amide. The additional peak at 534.3 eV can be associated to the presence of remnants of the spin finish emulsifier and possible contamination from adventitious carbon species in ambient air.



**Fig. S3**. XPS analysis unmodified aramid (v-UA). Experimental curve (dashed lines), curve envelop (dark solid line). a) N 1s spectra and functional groups assigned. c) O 1s spectra and functional groups assigned.

The C 1s spectra of PDA in Fig. 3b was fitted with three peaks, the first at 284.6 eV corresponding to the C=C and C-C bonds of polydopamine. The second peak at 286.3 eV was assigned to C-N and C-O bonds while the smallest peak at 289.6 was assigned to the C=O group in the quinone moiety and carboxylate units of PDA. Fig. S4a shows the three fitted curves of the N 1s spectra, the first one at a binding energy of 400.1 eV was assigned to the enamine group of PDA, while the peak at 401.7 was assigned to the primary amine. An additional peak was fitted at 403.1 eV and can arise from the protonated TRIS buffer used during the polymerization. This agrees with the identified presence of Cl atoms in Table 1. The best fit for the O 1s spectra was achieved with three peaks (Fig. S4 b), the first one at 531.8 eV corresponds to the oxygen of the quinone, the second peak at 533.6 eV was assigned

to the hydroxyl groups of the phenol moieties in PDA. In addition, the third curve with a peak at 538 eV can be related to oxygen in a carboxylic acid.

This indicates that, besides the expected features corresponding to the main structure of PDA; the additional signals at 289.6 eV (C 1s), 538 eV (O 1s) and 403.1 (N 1s) suggest the presence of C=OO<sup>-</sup> from carboxylic groups and <sup>+</sup>NH<sub>3</sub> species. Even though more seldomly reported, the formation of carboxyl containing units has also been suggested as possible monomeric units in the structure of polydopamine (Figure S1b and S1c). The positive charge on the amine moiety can be explained as part of a charged monomeric unit in PDA which agrees with Figure S1c or by the possible incorporation of the amine containing TRIS buffer solution into the PDA structure which has also been reported in other studies.<sup>7,8</sup>



**Figure S4.** XPS analysis polydopamine coated aramid (v-PDA). Experimental curve (dashed lines), curve envelop (dark solid line). a) N 1s spectra and functional groups assigned. c) O 1s spectra and functional groups assigned.

	Atomic ratios					
	O/C	N/C	N/O	Si/C		
UA	0.23±0.006	$0.084 {\pm} 0.003$	$0.37 \pm 0.02$	$0.022 \pm 0.002$		
PDA	0.27±0.019	$0.099 \pm 0.001$	$0.37 \pm 0.03$	$0.022 \pm 0.005$		
PDA- Si	0.43±0.031	0.007±0.001	0.017±0.002	0.113±0.005		

Table S1. Atomic ratios obtained by XPS.

#### Thermogravimetric analysis of aramid fibers

The thermogravimetric analysis showed that the thermal stability of the fibers was retained after functionalization (Figure 4e and Table S2). UA displayed a thermal decomposition onset at 532 °C and a main decomposition step at 582 °C which is in line with the reported values from the supplier.<sup>12</sup> After coating with polydopamine, no major changes were observed, although the onset of decomposition is shifted slightly towards a lower temperature of 528 °C. This can be attributed to the release of low molecular weight oligomeric structures and possible unadhered residues from the TRIS buffer.<sup>10,13,14</sup> After the condensation with the silane coupling agent, the onset of decomposition and the main decomposition steps shifted towards higher temperatures, 544 °C and 584 °C, respectively. Additionally, the residue at the end of the test increased to 54 wt.-% from the original 49 wt.-% for UA and 52 wt.-% for PDA. These observations can be attributed to the presence of the inorganic component of this coupling agent, and they further support that the condensation of the silane coupling agent, and they further support that the condensation of the silane coupling agents was achieved.

	Т <sub>5%</sub> °С	Т <sub>10%</sub> °С	T <sub>max</sub> °C	Residue <sub>@700 °C</sub> wt%
UA	$532.4\pm5.7$	$558.8 \pm 1.4$	$582.1\pm0.3$	$48.7\pm0.3$
PDA	$528.2\pm8.8$	$561.9\pm1.3$	$583.3\pm0.3$	$52.1\pm0.9$
PDA-Si	$544.4\pm0.9$	$564.5\pm0.6$	$583.8\pm 0.4$	$54.2\pm1.2$

**Table S2.** Summary of thermogravimetric analysis of aramid fibers.

#### Single fiber tensile test

The results from single fiber tensile tests demonstrated that the mechanical properties of UA were preserved. The typical stress-strain curves obtained are shown in Figure 4f and a summary of the overall results are depicted in Table S3. The mechanical properties of unmodified aramid fibers,  $(3.6 \pm 0.2 \%$  strain at break, Modulus  $110.1 \pm 8.1$  GPa and tensile stress of  $3.41 \pm 0.4$  GPa) agree with the properties reported by the supplier and reported elsewhere. <sup>12,15</sup> In comparison, the obtained tensile strain at break, modulus, and tensile stress at break of PDA-Si fibers were  $3.4 \pm 0.5 \%$ ,  $108.4 \pm 6.8$  GPa and  $3.3 \pm 0.5$  GPa, respectively, which are almost identical to the values measured for UA.

	Madulua	Tensile	strain	at Tensile	stress	at
	Modulus	break		break		
	(GPa)	(%)		(GPa)		
UA	$110.1 \pm 8.1$	$3.6\pm0.2$		$3.4\pm0.4$		
PDA	$103.2\pm13.6$	$3.4\pm0.5$		$3.1\pm 0.8$		
PDA-Si	$108.4\pm6.8$	$3.4\pm0.5$		$3.3\pm0.5$		

Table S3. Mechanical properties of aramid fibers tested by single fiber tensile tests.

Proposed mechanism of the curing reaction of tri-epoxy resin with citric acid



**Fig. S5**. Steps for the acid catalyzed ring opening of the epoxy resin with citric acid and potential side reactions with water.



**Fig. S6.** Acquired ATR-FTIR spectra of the uncured TGE resin, aqueous solution of citric acid and cured thermoset. A comparison with the ATR-FTIR spectra of the composites is depicted in Figure S10.





Fig. S7. a) Curing behavior and b) glass transition temperature of cured thermoset.



Fig. S8. Thermal properties of virgin thermoset and composites.

	T <sub>5%</sub>	T <sub>10%</sub>	$T_{\text{main}}$	Residue <sub>DTG</sub>	Residue <sub>500 °C</sub>	Residue <sub>700°C</sub>
TVx	$268.3 \pm 3.7$	311.5 ± 1.5	$367.5\pm4.4$	49.4 3.3 ± 1.3	5.7 ± 1.8	$4.5\pm1.4$
UA <sub>composite</sub>	$285.5 \pm 10.5$	$330.7\pm4.8$	$370.50 \pm 0.2$	$73.3 \pm 3.7$	$49.2\pm 6.6$	$24.7\pm3.5$
PDA <sub>composite</sub>	$287.0 \pm 1.2$	$330.5\pm1.3$	$374.7\pm2.8$	$72.5\pm2.3$	49.6 ± 1.8	$25.0\pm0.2$
PDA-Si <sub>composite</sub>	284.03 ± 1.3	$330.2 \pm 1.3$	$375.0\pm0.1$	$70.8\pm1.1$	45.1 ± 2.2	23.6 ± 1.1

Table S4. Thermogravimetric analysis of virgin thermoset (TVx) and composites.

### **Chemical recycling**

Acidic hydrolysis in a solution of 1M HCl did not lead to the dissolution of the virgin thermoset (Figure S9a) and solid pieces of the thermoset were still observed after 24 h of reaction. ATR-FTIR spectra confirmed that the characteristic bands from the virgin thermoset were unchanged (Fig. S9b).



Figure S9. Hydrolysis in acidic conditions.

Interestingly, the hydrolysis reaction in a solution of 1M NaOH resulted in complete dissolution of the thermoset in just 30 minutes. The solubilized thermoset consisted of an immiscible liquid which, after neutralization, separation and drying, generated the formation of small crystals and a viscous resin (Figure S10a). The disappearance of the bands at 1730 cm<sup>-1</sup> and 1181 cm<sup>-1</sup> associated to the ester bonds and the appearance of bands corresponding to secondary and primary alcohols and carboxylates suggests that the hydrolysis of the ester bond took place (Figure S10b). The large contrast among the outcomes from the hydrolysis in acidic and basic conditions is in line with other studies which have reported the higher susceptibility of ester based thermoset and thermoplastic matrixes towards base hydrolysis.<sup>16–20</sup> Despite the clear success of basic hydrolysis to dissolve TVx, this method was not pursued further as the recycling conditions proved to be very detrimental to the aramid fibers (Fig. S11).



**Fig. S10.** Hydrolysis in basic conditions. Characterization from degradation products suggests the formation of a mixture of oligomeric structures rich in carboxylates and alcohol groups. The viscous resin presented new bands around 1637 cm<sup>-1</sup>, 1595 cm<sup>-1</sup>, and 1272 cm<sup>-1</sup> associated with the C=O stretching and <sup>-</sup>O-C=O stretching vibrations from carboxylates. The bands at 3350 cm<sup>-1</sup>,1085 cm<sup>-1</sup> and 1043 cm<sup>-1</sup> were assigned correspond to the H-O, C-O and C-OH stretches from alcohol groups. The crystals presented bands at 1708 cm<sup>-1</sup> and 1571 cm<sup>-1</sup>, which were assigned to O=C stretching vibrations and at 1363 and 1223 which correspond to HO-C=O stretching vibrations from carboxylic acids.



**Fig. S11.** Comparison between the recovered PDA-Si meshes after chemical recycling in a) basic hydrolysis and b) solvolysis through transesterification. The meshes presented the clear loss of the functionalization by the basic hydrolysis method. This was corroborated by SEM images which evidenced the c) loss of the characteristic surface morphology by chemical recycling with NaOH and d) the retention of the functionality through transesterification.



**Fig. S12**. a) SEC elugram of the recycled TRx resin. b) DSC thermogram depicting residual exotherm at 97 °C corresponding to the curing reaction of TRx.



**Fig. S13**. Spectroscopic characterization of the viscous resin performed in deuterated DMSO by <sup>13</sup>C NMR.



**Fig. S14**. a) Typical stress-strain curve b) tensile stress and c) tensile strain values of virgin thermoset (TVx), recycled thermoset (TRx) and thermoset with 50/50 wt.-% virgin/recycled thermoset (TVx<sub>50</sub> TRx<sub>50</sub>).



Fig. S15. a) Spectroscopic characterization of the recycled TRx and its comparison with TVx spectra. b) Proposed TRx structure. c) DSC thermogram of TRx and TVx depicting a reduced  $T_g$  after chemical recycling.



Fig. S16. Thermal properties of virgin TVx and recycled TRx thermoset.

 Table S5. Thermal stability of virgin thermoset (TVx) and recycled thermoset (TRx).



**Figure S17.** Comparison of the ATR-FTIR spectroscopic characterization of virgin unmodified aramid (v-UA), virgin polydopamine coated aramid (v-PDA) and recycled polydopamine coated aramid (r-PDA). The spectra suggest that the PDA coating did not withstand the chemical recycling conditions; the characteristic C=O band at 1612 cm<sup>-1</sup>, associated to the conjugated imine structure in polydopamine, and the band associated to C-NH stretching vibrations from amine groups at 1473 cm<sup>-1</sup> is no longer present after the chemical recycling treatment.



Fig. S18. SEM images of fibers after Soxhlet extraction a) PDA coated fibers b) PDA-Si fibers

Table S6. Atomic percentage determined by SEM-EDS before and after Soxhlet extraction

	С	0	Ν	Si
	(wt%)	(wt%)	(wt%)	(wt%)
PDA before extraction	$75.2\pm3.3$	$16.2 \pm 1.2$	$8.5\pm1.0$	$0.1 \pm 0.1$
PDA after extraction	76.1 ± 1.1	$15.8\pm0.4$	$7.8 \pm 1.2$	$0.3\pm0.2$
PDA-Si before	$64.6\pm2.6$	$25.5\pm2.7$	$4.3\pm2.0$	$5.5 \pm 1.7$
PDA-Si after extraction	$70.7\pm2.3$	$19.8\pm2.3$	$4.4\pm3.0$	5.1 ± 1.6



**Fig. S19.** Typical lap shear curves comparing a) the performance of virgin meshes and recycled thermoset and b) the performance of recycled meshes with virgin thermoset,

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