Supporting Information

Aramid Nanofiber Templated *In situ* S_NAr Polymerization for Maximizing the Performance of All-Organic Nanocomposites

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Experimental Procedures

Materials

Bisphenol-A (BPA, 99%) and bis(4-fluorophenyl) sulfone (DFPS, 99%) were purchased from TCI (Tokyo, Japan) and recrystallized in methanol. Potassium carbonate (K₂CO₃, 99%, Sigma-Aldrich, USA) was ground into a fine powder and subsequently dried with phosphorus pentoxide under vacuum. Potassium hydroxide (KOH, 90%), dimethyl sulfoxide (DMSO, 99.7%), *N*,*N*'-dimethylacetamide (DMAc, 99.8%), acetic acid (HPLC grade), methanol (HPLC grade), 18-crown-6 (99%), chloroform (HPLC grade), and dioctyl terephthalate (DOT, 96%) were purchased from Sigma-Aldrich. Kevlar[®] thread was sourced from Dupont Inc. (USA).

Preparation of the ANF/DMSO solution

Kevlar (0.20 g), KOH (0.30 g), and DMSO (100 mL) were loaded to a 250 mL dried roundbottom flask (RBF) and magnetically stirred at 25 °C. The solution gradually turned dark red and complete dissolution was achieved without any sludge after approximately 180 h. The concentration of ANF/DMSO solution was 0.2 w/v%.

Synthesis of polysulfone (PSU)

BPA (4.68 g, 20.5 mmol), DFPS (5.21 g, 20.5 mmol), and K_2CO_3 (3.55 g, 25.7 mmol) were added to a dried glass flask equipped with mechanical stirrer and Dean-Stark apparatus. Subsequently, 0.05 molar equivalents of 18-crown-6 (0.271 g, 1.02 mmol) against diols, and DMSO (34 ml, 29 w/v% to the monomer content) were added to the flask under a dry nitrogen atmosphere. The reaction mixture was bath sonicated for 10 min (60 Hz, Mujigae, Korea) and subsequently heated for 4 h at 155 °C under a mild nitrogen flow. After polymerization, the mixture was cooled to room temperature and precipitated in a water/methanol mixture (1 L, 50/50 vol%) containing acetic acid (10 mL). To remove residual additives, the solid was filtered and re-precipitated after dissolution in DMAc. The precipitated polymer was filtered and washed with deionized water and methanol. The polymer was dried under vacuum at 80 °C for 24 h. Theoretical polymer product (9.07 g); final polymer product (8.71 g, 96%); M_w : 164,200 g mol⁻¹; PDI: 1.84; ¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.82–7.81, 7.25-7.20, 6.98-6.97, 6.92-6.90,1.67.

In situ synthesis of PSU-I-0.075

The same synthetic procedure for PSU was conducted except the reaction media of DMSO (3.4 mL) was replaced with an ANF/DMSO solution (0.2 wt/v%, 3.4 mL) for the target ANF (6.8 mg) per theoretical polymer (9.07 g) set to 0.075 wt%. The total amount of DMSO was fixed at 34 mL. Final polymer product (8.80 g, 97%); M_w : 136,500 g mol⁻¹; PDI: 1.87.

In situ synthesis of PSU-I-0.15

The same synthetic procedure as for PSU was performed except DMSO (6.8 mL) was replaced with an ANF/DMSO solution (0.2 w/v%, 6.8 mL) for the target ANF (13.6 mg) per theoretical polymer (9.07 g) set to 0.15 wt%. Total amount of DMSO was fixed at 34 mL. Final polymer product (8.71 g, 96%); M_w : 160,200 g mol⁻¹; PDI: 1.69.

In situ synthesis of PSU-I-0.75

The same synthetic procedure as for PSU was performed in an ANF/DMSO solution (0.2 w/v%, 34 mL) for the target ANF (68.0 mg) per theoretical polymer (9.07 g) set to 0.75 wt%. Final polymer product (8.71 g, 96%); M_w : 182,300 g mol⁻¹; PDI: 1.87.

Model in situ polymerization of PSU-I-2

First, 2 wt% ANF was dispersed in PSU to investigate chemical grafting on the ANF surface. BPA (3.10 g, 13.56 mmol), DFPS (3.45 g, 13.56 mmol), and K₂CO₃ (2.34 g, 16.95 mmol) were added to a dried glass flask equipped with mechanical stirrer and Dean-Stark apparatus. Then, 0.05 molar equivalents of 18-crown-6 (0.18 g, 0.68 mmol) against diols, and ANF/DMSO solution (0.2 w/v%, 60 mL) for the target ANF (0.12 g) per theoretical polymer (6.0 g) set to 2.0 wt% were added to the flask under a dry nitrogen atmosphere. The reaction mixture was bath sonicated for 10 min and heated for 4 h at 155 °C under a mild nitrogen flow. After polymerization, the mixture was cooled to room temperature and precipitated in a water/methanol mixture (1 L, 50/50 vol%) containing acetic acid (10 mL). To remove residual additives, the solid was filtered and re-precipitated after dissolution in DMAc. The precipitated polymer was filtered and washed with deionized water and methanol. The polymer was dried under vacuum at 80 °C for 24 h.

To remove the homo-polymer by washing, the dried sample (**PSU-I-2**, 6 g) was dissolved in chloroform (500 mL) and magnetically stirred for 3 h, and subsequently bath sonicated for 20 min. The sample solution was filtered and dried under vacuum at 80 °C for 24 h. The above washing process was repeated 5 times depending on the experiment.

Preparation of solution-casted film

In situ polymer nanocomposite solutions were prepared by dissolving the PSU-I-series in DMAc to a final concentration of 7.5 wt%. In contrast, the blended polymer nanocomposite solutions were prepared by dissolving PSU in DMAc and mixing with an ANF/DMSO (0.2 wt%) solution to target an ANF per PSU ratio of 0.075–0.75 wt%. The total amount of polymer per polar aprotic solvents was fixed at 7.5 wt%. The mixed solution was mildly stirred at 80 °C

for 12 h and subsequently bath sonicated for 20 min. Each solution was poured into an aluminum dish and dried at 100 °C in a convection oven for 2 d.

Preparation of the hot-pressed film

To reduce the roughness of the fabricated films for thermomechanical annealing, the films were hot-pressed at 200 °C under 100 bar for 5 min.

Preparation of the injection molded specimen

For the *in situ* nanocomposite specimens, the PSU-I-series and DOT (10 wt% per PSU) were dissolved in DMAc (10 wt%) at 80 °C for 1 h. For the blended nanocomposite specimens, neat PSU, DOT (10 wt% per PSU), and ANF/DMSO were dissolved in DMAc (10 wt% per total solvent) at 80 °C for 12 h and subsequently bath sonicated for 20 min. Each solution was subsequently dried at 100 °C in a convection oven for 3 d. The prepared powder was melted at 270 °C for 8 min, and then injection molded into a dumbbell-shaped specimen, with a length, width, and thickness of 63.50, 3.18, and 3 mm, respectively, using a HaakeTM Minijet (Thermo Scientific, Waltham, MA, USA). The cylinder temperature, injection pressure, filling time, and mold temperature were 290 °C, 500 bar, 15 s, and 230 °C, respectively.

Chemical and thermal characterizations

The ¹H NMR spectra were obtained using a Bruker AVANCE 300-MHz spectrophotometer (Billerica, MA, USA) with the samples dissolved in CDCl₃. Cross polarization/magic angle spinning (CP/MAS) ¹⁵N NMR experiments were conducted using a 400 MHz (9.4 T) Bruker Avance spectrometer (Avance III HD 400, Bruker, USA) with a 4 mm HX-MAS probe at a ¹⁵N frequency of 40.56 MHz. The samples were packed into 4 mm diameter zirconia rotors

and spun at 10 kHz at the magic angle. The CP/MAS ¹⁵N NMR experiments were performed with a contact time of 2000 s, 90°, ¹H Pulse width of 2.6 ms, and repetition delays of 5 s. The number of scans for the accumulation of the solid-state CP/MAS ¹⁵N NMR spectra was 40 x 10³. The chemical shifts of ¹⁵N are reported relative to ammonium chloride (0 ppm). The number-average molecular weight (M_n) , weight-average molecular weight (M_w) , and polydispersity index (PDI) were determined by gel permeation chromatography (GPC) with an ACQUITY refractive index detector using chloroform as a mobile phase flowing at a velocity of 0.6 mL min⁻¹. ACQUITY APC XT columns (mixed bed, maximum pore size 450 Å, Waters Corp., Milford, MA, USA) were maintained at 40 °C during the measurements. The universal calibration was based on polystyrene standards. Differential scanning calorimetry (DSC; Q-2000, TA Instruments, USA) measurements were conducted from 30 to 280 °C under a nitrogen atmosphere at a heating/cooling rate of 10 °C min⁻¹. Raman spectra were collected using a confocal Raman microscope (LabRamHR, Horiba Jobin-Yvon, France) fitted with a 100× objective (spot size $\sim 1 \mu m$). The samples were excited using a diode laser (785 nm) with a grating of 600 gr/mm (spectral resolution ~ 1.3 cm⁻¹) in regular mode. Measurements were performed at two different polarized laser beam orientations with respect to the flow direction of the samples. In the first configuration, the flow direction was parallel (0°) to the polarized beam direction, whereas in the second configuration, the orientation was perpendicular (90°). The alignment in the composite was determined by comparing the spectra of the parallel and perpendicular directions. Fourier-transform infrared (FTIR) spectra were recorded using a Nicolet iS50 spectrometer (Thermos-Fisher Scientific, USA) with a resolution of 0.4 cm^{-1} at 650–4000 cm^{-1} for a total of 128 scans per analysis. The samples were measured in the vertical attenuated total reflection (ATR) accessory containing a diamond-ZnSe crystal and the infrared beam angle of incidence was 45°. X-ray photoelectron spectroscopy (XPS) signals were recorded using a Thermo

Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK) equipped with a microfocused monochromatic Al $K\alpha$ X-ray source (1486.6 eV). A 400 μ m X-ray beam was used at 6 mA × 12 kV. The spectra were acquired in constant analyzer energy mode with a pass energy of 50 eV. A pass energy of 50 eV was chosen as a compromise value, providing a satisfactory energy resolution and reasonably high sensitivity/transmission. The spectra were recorded in standard lens mode with pass energy of 50 eV and a total of 20 scans.

Mechanical and structural characterizations

The tensile properties were measured using a universal testing machine (UTM; Instron High Wycombe, UK) at a drawing rate of 10 mm min⁻¹, according to ASTM D638-03. The films were cut into dumbbell-shapes with a length, width, and thickness of 63.50, 3.1, and 65–80 μ m, respectively, using a jockey-type cutting machine.

SAXS measurements were carried out using synchrotron radiation at the 9A beam line, Pohang Accelerator Laboratory. The wavelength (λ) of the incident X-ray beam was 0.128 nm ($\Delta\lambda/\lambda = 10^{-4}$) and the sample-to-detector distance was set as 1 m. An airtight aluminum sample cell having two Kapton windows was designed to prevent water contamination during the measurements. The resulting two-dimensional scattering data were averaged azimuthally to obtain 1-dimensional intensity plot versus *q*.

A field-emission scanning electron microscopy (SEM; Hitach SU-8220, Japan) with a secondary electron detector was used to observe the morphology of the ANF/PSU nanocomposite after tensile testing at the cross-sectional area of fracture. The samples were coated with a thin layer of Pt (~7 nm) using a K575X sputtering coater (Emitech, UK) operated at 20 mA for 45 s before SEM observation. To evaluate the composite internal structure in three-dimensions (3D), i.e. the fiber distribution, X-ray micro-computed tomography (µCT) was used (SkyScan 1176, Bruker-micro CT, Belgium). The X-ray source

applied voltage and current were 40 kV and 398 μ A, respectively. The generated 3D images were recorded with a rotation of 0.3° by rotating the sample 360°. The total sample scan time was approximately 1 h for each sample. After scanning, the 3D images were reconstructed with Dataviewer software and the reconstructed images were processed with CT vox software (Bruker-micro CT, Belgium). The measured samples with a length, width, and thickness of 0.5, 0.5, and 3 mm, respectively, were cut from the tensile tested dumbbell-shaped samples of the grip section. The rheological measurements for investigating the stress dissipation behavior of the molten ANF/PSU composites were performed at 290 °C using an Anton Paar MCR 302 rheometer (Anton Paar, Austria) with a parallel-plate geometry (plate diameter of 25 mm) and a gap of approximately 1 mm. The complex viscosity (η^*), storage modulus (G'), and loss modulus (G'') were measured using a frequency sweep over an angular frequency (ω) range of 0.1 to 100 rad s⁻¹.



Figure S1. Illustration of the preparation of the ANF/DMSO solution and the corresponding AFM image (height-mode).



Figure S2. Photographs of samples of (1) ANF in DMSO, (2) precipitation in methanol, (3) filtration and sonication in fresh DMSO.

Table S1. Preparation information for the nanocomposites and calculation of ANF content per nanocomposite.

In situ method					Blending method				ANF content ^e	
Code	Feed ^a				Theoretical	Code	Feed ^a			(wt%)
	$BPA^{b}(g)$	DFPS ^b (g)	ANF ^c (mg/mL DMSO)	DMSO (mL)	(g)		ANF ^c (mg/mL DMSO)	DMSO (mL)	PSU	
PSU	4.68	5.21	0	34.0	9.07					0
PSU-I-0.075	4.68	5.21	6.80/3.4	30.6	9.07	PSU-B- 0.075	6.80/3.4	30.6	9.07	0.075
PSU-I-0.15	4.68	5.21	13.61/6.8	27.2	9.07	PSU-B- 0.15	13.61/6.8	27.2	9.07	0.15
PSU-I-0.75	4.68	5.21	68.03/34.0	0	9.07	PSU-B- 0.75	68.03/34.0	0	9.07	0.75

^{*a*}Additionally fed chemicals for polymerization were 18-crown-6 (5 mol% per BPA), K₂CO₃ (125 mol% per BPA), and DMSO (total amount: 29 w/v% for monomer weights). ^{*b*}BPA and DFPS were fed with equal molar ratios.

^oPristine concentration of the prepared ANF/DMSO solution was 0.2 g per 100 mL DMSO.

^dCalculated by the sum of weights of the repeating monomer-unit.

^eBased on the weight percentage of ANF fed per theoretical PSU product

The wt% of ANF per PSU was estimated using the theoretical weight of ANF per PSU while

considering the respective monomer feed. For example, the 0.2 w/v% ANF/DMSO solution of

3.4 mL contained 6.80 mg ANF and 4.68 g of BPA, which produced 9.07 g of PSU. The wt%

of ANF was 0.075.

Samples	ANF content ^a (wt%)	$M_{\mathrm{n}}{}^{b}$ (kg mol ⁻¹)	$M_{\mathrm{w}}{}^{b}$ (kg mol ⁻¹)	PDI ^b	$T_{g}^{c}(^{\circ}\mathrm{C})$
PSU ^d	0	89	164	1.84	195
PSU-I-0.075	0.075	73	137	1.87	197
PSU-I-0.15	0.15	95	160	1.69	196
PSU-I-0.75	0.75	97	182	1.87	199

Table S2. Characterizations of PSU samples prepared from *in situ* polymerization.

^{*a*}Based on the weight percentage of ANF fed per theoretical amount of PSU product. ^{*b*}Determined by CHCl₃-GPC using polystyrene standards (RI detector).

^cMeasured by DSC at a heating rate of 10 °C min⁻¹ (2nd scan).

^dNeat PSU was used to prepare the blended polymer nanocomposites (**PSU-B** series).



Figure S3. Tensile stress-strain curves of the neat PSU prepared by solution casting, hotpressing, and injection molding methods.

Preparation method	ANF content (wt%)	Sample code	Young's modulus (GPa)	Ultimate tensile strength (MPa)	Elongation at break (%)	Toughness (MJ m ⁻³)	Increased toughness ratio
In situ	0.75	PSU-I-0.75	2.9 ± 0.1	66 ± 1	3.0 ± 0.1	1.13 ± 0.05	3.0
	0.15	PSU-I-0.15	2.6 ± 0.1	43 ± 3	2.2 ± 0.2	0.57 ± 0.08	1.5
	0.075	PSU-I-0.075	2.9 ± 0.1	50 ± 1	2.4 ± 0.1	0.71 ± 0.06	1.9
-	0	PSU	2.4 ± 0.1	36 ± 4	1.8 ± 0.1	0.38 ± 0.06	-
Blending	0.075	PSU-B- 0.075	2.4 ± 0.2	44 ± 4	2.4 ± 0.1	0.62 ± 0.10	1.6
	0.15	PSU-B-0.15	2.9 ± 0.1	54 ± 1	2.9 ± 0.0	0.99 ± 0.03	2.6
	0.75	PSU-B-0.75	2.4 ± 0.1	40 ± 1	2.1 ± 0.0	0.50 ± 0.02	1.3

Table S3. Tensile properties of the nanocomposite films prepared by solution casting.



Figure S4. Ultimate tensile strength (UTS) and toughness of the nanocomposite films prepared by solution casting.

by hot pressing. ANF content Ultimate Preparation Sample code Young's Elongation at Toughness Increased method (wt%) modulus tensile break (%) $(MJ m^{-3})$ toughness (GPa) strength ratio (MPa)

 54 ± 2

 47 ± 2

 53 ± 5

 51 ± 3

 61 ± 3

 51 ± 4

 42 ± 2

 3.8 ± 0.3

 3.8 ± 0.3

 8.1 ± 0.6

 7.6 ± 0.4

 3.6 ± 0.4

 2.6 ± 0.4

 2.3 ± 0.1

 1.40 ± 0.15

 1.91 ± 0.41

 2.90 ± 0.32

 2.64 ± 0.11

 1.38 ± 0.18

 0.84 ± 0.22

 0.59 ± 0.02

0.53

0.72

1.1

-

0.52

0.32

0.22

 2.7 ± 0.1

 2.9 ± 0.0

 2.9 ± 0.1

 3.0 ± 0.1

 3.0 ± 0.1

 2.9 ± 0.1

 2.9 ± 0.1

0.75

0.15

0.075

0.075

0.15

0.75

0

In situ

Blending

PSU-I-0.75

PSU-I-0.15

PSU-I-0.075

PSU-B-0.075

PSU-B-0.15

PSU-B-0.75

PSU

Table S4.	. Tensile prop	perties of the nar	nocomposite	films prepa	ared by solu	tion casting	followed



Figure S5. UTS and toughness of the nanocomposite films prepared by solution casting followed by hot pressing.



Figure S6. Polarized Raman spectrum of (a) PSU, (b) **PSU-B-0.15**, (c) **PSU-I-0.15**, and (d) comparison of polarized Raman intensity ratio of 0° with respect to that of 90°.

Polarized Raman data can support the orientation of PSU chains with respect to the injection direction. Overall, the peak intensity of the parallel spectra was much higher than that of the cross spectra because of the injection-induced chain alignment and the PSU bonds. By comparing the intensity ratio of the most visible peak at C-(=)C stretching, chemical bond ordering increased successively as follows: neat PSU, blended PSU, *in situ* prepared PSU nanocomposite.

Preparation method	ANF content (wt%)	Sample code	Young's modulus (GPa)	Ultimate tensile strength (MPa)	Elongation at break (%)	Toughness (MJ m ⁻³)	Increased toughness ratio
In situ	0.75	PSU-I-0.75	2.1 ± 0.0	88 ± 3	15.3 ± 1.6	10.1 ± 0.9	2.1
	0.15	PSU-I-0.15	2.2 ± 0.1	79 ± 5	26.6 ± 2.7	16.4 ± 1.8	3.4
	0.075	PSU-I-0.075	2.1 ± 0.1	57 ± 1	14.3 ± 0.4	7.06 ± 0.29	1.5
-	0	PSU	2.0 ± 0.0	48 ± 0	12.7 ± 0.2	4.85 ± 0.08	-
Blending	0.075	PSU-B-0.075	2.0 ± 0.1	49 ± 14	3.8 ± 1.1	1.29 ± 0.56	0.27
	0.15	PSU-B-0.15	2.3 ± 0.1	24 ± 2	1.7 ± 0.2	0.25 ± 0.04	0.05
	0.75	PSU-B-0.75	1.9 ± 0.1	61 ± 14	4.9 ± 1.0	2.04 ± 0.77	0.42

Table S5. Tensile properties of the nanocomposite films prepared by injection molding.





Figure S7. UTS and toughness of the nanocomposite films prepared by injection molding.

Table S6. Molecular weight variations of PSU after blending and injection molding.

Sample	$M_{n^{a}}$ (kg mol ⁻¹)	$M_{\rm w}^a$ (kg mol ⁻¹)	PDI ^a
PSU (1)	89	164	1.84
PSU (2) after blending of PSU (1) with	82	172	2.08
plasticizer	81	172	2.11
PSU (3) after injection molding of PSU (2)	83	165	1.99
	82	166	2.01

^{*a*}Determined by CHCl₃-GPC using polystyrene standards (RI detector).



Figure S8. Differential thermogravimetric analysis curves of polymer and nanocomposites. - As expected, the maximum decomposition temperatures (T_{max}) of samples were around 537~542 °C, which are far above the melt-processing temperature of 270 °C.



Figure S9. The 1D and 2D SAXS profiles of PSU-I-0.15 at different measurement spots on the fractured specimen.



Figure S10. The 1D and 2D SAXS profiles of PSU-B-0.15 at different measurement spots on the fractured specimen.



Figure S11. (a) Observed fractured surface marked as a red line for SEM analysis. (Frontal) SEM images of (b) PSU-I-0.75, and (c) PSU-B-0.75. (Oblique) SEM images of (d) PSU, (e) PSU-I-0.15, and (f) PSU-B-0.15 (scale bar: 1 mm).



Figure S12. Exemplary perforations of a stamp.



Figure S13. Magnified SEM images of (a) PSU, (b) PSU-I-0.15, (c) PSU-B-0.15, (d) PSU-I-

0.75, and (e) PSU-B-0.75 (scale bar: 50 μm).



Figure S14. A magnified SEM image of PSU-I-0.15 (scale bar: 50 µm).



Figure S15. ATR-FTIR spectra of neat PSU and ANF samples.



Figure S16. XPS spectra of the N1s region of the two composite systems after five washing cycles.



Figure S17. CP/MAS ¹⁵N NMR spectra of pristine ANF, and PSU-B-2 and PSU-I-2 after 5

cycles of washing.