Supporting Information

Anisotropic Alignment of Bacterial Nanocellulose Ionogels for Unconventionally High Combination of Stiffness and Damping

*Wonseok Choi[1], Amith Abraham[1], Jongkuk Ko[2], Jeong Gon Son[3,4], Jinhan Cho[2,4], Byoung-In Sang[1], Bongjun Yeom[1]**

[1]Department of Chemical Engineering, Hanyang University Seoul 04763, Republic of Korea.

[2]Department of Chemical and Biological Engineering, Korea University, Seoul 02841, Republic of Korea.

[3]Soft Hybrid Materials Research Center, Korea Institute of Science and Technology (KIST), Seoul 02792, Republic of Korea.

[4]KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 02841, Republic of Korea.

Corresponding Author: *byeom@hanyang.ac.kr

Table S1. Summary of the nanocellulose based ionogel films in previous studies.

Ref	Materials	Fabrication method	IL content	Elastic modulus	Ionic conductivity	alignment
Our work	Bacterial cellulose (BC)/ $EMImBF_4$	Wet-stretching the BC hydrogel and reswelling in IL.	47 vol%	28 GPa	0.23 mS cm^{-1} (30 °C)	O
(S1)	Cotton cellulose/ BMImCl	Immersing the cellulose/BMImCl solution in water.	40 wt%	30 MPa	-	X
(S2)	Microcrystalline cellulose (MCC)-SiO_2/ EMImAc	Casting the MCC-SiO_2/ EMImAc solution	82 wt%	0.7 MPa	1 mS cm^{-1} (30 °C)	X
(S3)	Microcrystalline cellulose (MCC)/BMImCl	Casting and curing the MCC/BMImCl solution	87 wt%	0.42 MPa	-	X
(34)	Bacterial cellulose (BC)/ EMImDCA, $EMImTf_2N$, $EMImBF_4$	Immersing the BC alcogel in ILs and drying	95 wt%	0.09 MPa	28 mS cm^{-1} (25 °C)	X
(81)	Chitosan-cellulose/ EMImAc	Gelation the chitosan-cellulose/EMIMAc solution.	91 wt%	0.001 MPa	2.1 mS cm^{-1} (25 °C)	X
(82)	Methylcellulose (MC)/PYR-$_{14}$TFSI	Gelation the MC/ PYR_{14}TFSI solution	50 wt%	2.0 GPa	0.0056 mS cm^{-1} (30 °C)	X

(Ref. S1) Haq, M. A.; Habu, Y.; Yamamoto, K.; Takada, A.; Kadokawa, J. ichi. Ionic Liquid Induces Flexibility and Thermoplasticity in Cellulose Film. *Carbohydr. Polym.* **2019**, *223*, 115058.

(Ref. S2) Song, H.; Luo, Z.; Zhao, H.; Luo, S.; Wu, X.; Gao, J.; Wang, Z. High Tensile Strength and High Ionic Conductivity Bionanocomposite Ionogels Prepared by Gelation of Cellulose/Ionic Liquid Solutions with Nano-Silica. *RSC Adv.* **2013**, *3*, 11665–11675.

(Ref. S3) Kunchornsup, W.; Sirivat, A. Physically Cross-Linked Cellulosic Gel via 1-Butyl-3-Methylimidazolium Chloride Ionic Liquid and Its Electromechanical Responses. *Sensors Actuators, A Phys.* **2012**, *175*, 155–164.

Table S2. Atomic ratio of BC and ionogel samples.

Sample	Atomic ratio (%)				
	B 1s	C 1s	N 1s	O 1s	F 1s
Pristine BC	-	61.5	2.6	35.9	-
BC/IL	6.8	54.1	9.8	10.6	18.7
Aligned BC	-	58.2	2.3	39.5	-
Aligned BC/IL	8.9	46.9	12.0	3.4	28.3

Table S3. Deconvoluted peak ratio of BC and BC ionogel samples.

Sample	Deconvoluted peak ratio (%)						
	C 1s				O 1s		
	C1	C2	C3	C4	O1	O2	O3
Pristine BC	30.7	48.9	20.4	-	6.7	66.4	26.9
BC/IL	32.8	36.6	5.8	24.9	6.8	57.1	36.1
Aligned BC	20.2	46.3	33.5	-	5.1	81.8	13.2
Aligned BC/IL	29.8	44.7	4.3	21.2	3.9	55.2	40.9

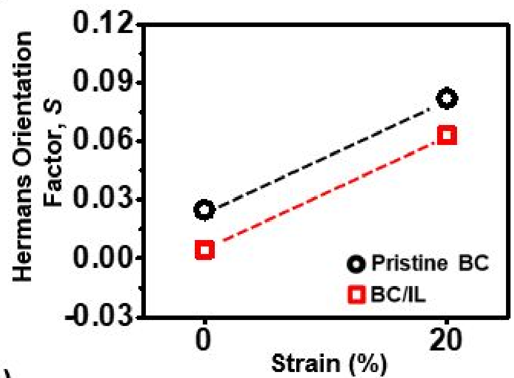
Table S4. Summary table for VFOM values of BC and ionogel samples.

VFOM (E*·tan δ)									
Sample	-100 °C	-50 °C	-25 °C	0 °C	5 °C	25 °C	50 °C	100 °C	150 °C
Pristine BC	0.57±0.13	0.65±0.14	0.62±0.11	0.61±0.24	0.59±0.15	0.56±0.12	0.53±0.07	0.54±0.05	0.57±0.07
Aligned BC	0.47±0.12	1.1±0.2	1.0±0.3	1.3±0.3	1.2±0.4	0.6±0.2	0.54±0.11	0.48±0.10	0.43±0.10
BC/IL	1.1±0.1	1.3±0.1	1.2±0.3	1.1±0.3	1.1±0.3	1.0±0.3	0.93±0.14	0.96±0.11	1.0±0.1
Aligned BC/IL	0.88±0.10	1.5±0.2	2.3±0.2	2.4±0.3	2.3±0.2	1.2±0.2	1.2±0.2	1.0±0.2	0.94±0.12

Table S5. Comparison table for various types of ionogels with material parameters. The same data points are utilized to plot Figure 7b.

Sample	IL content	Storage modulus (Pa)	Ionic conductivity ($mS\ cm^{-1}$)
BC/IL (This work)	70 vol%	6.7×10^{9} (20 °C) 7.3×10^{9} (60 °C)	0.13 (20 °C) 0.27 (60 °C)
Aligned BC/IL (This work)	48 vol%	1.9×10^{10} (20 °C) 1.7×10^{10} (60 °C)	0.16 (20 °C) 0.45 (60 °C)
BCIG/EMImDCA (Ref 34)	95 wt%	2.5×10^{4} (25 °C)	28.8 (25 °C)
PMMA/EMITFSI (Ref 73)	20 wt%	1.6×10^{6} (60 °C)	0.158 (60 °C)
PEO-CTA/BMITFSI (Ref 78)	21 vol%	8×10^{8} (50 °C)	0.6 (50 °C)
F127/IL/Oil (Ref 79)	20 wt%	1×10^{6} (70 °C)	3.0 (70 °C)
Chitosan/cellulose (Ref 80)	91 wt%	1×10^{3} (25 °C)	2.1 (25 °C)
MC/PYR14TFSI (Ref 81)	50 wt%	2.0×10^{9} (30 °C)	0.0056 (30 °C)
SOS/$BMImPF_6$ (Ref 82)	90 wt%	1×10^{3} (10 °C)	0.006 (60 °C)

(a)



(b)

	< $\cos^2\theta$>	S
Pristine BC	0.35	0.025
BC/IL	0.34	0.0046
Aligned BC	0.39	0.082
Aligned BC/IL	0.38	0.063

Figure S1. (a) Hermans orientation factor of BC and ionogel samples before and after alignment, and (b) calculated parameters for various samples.

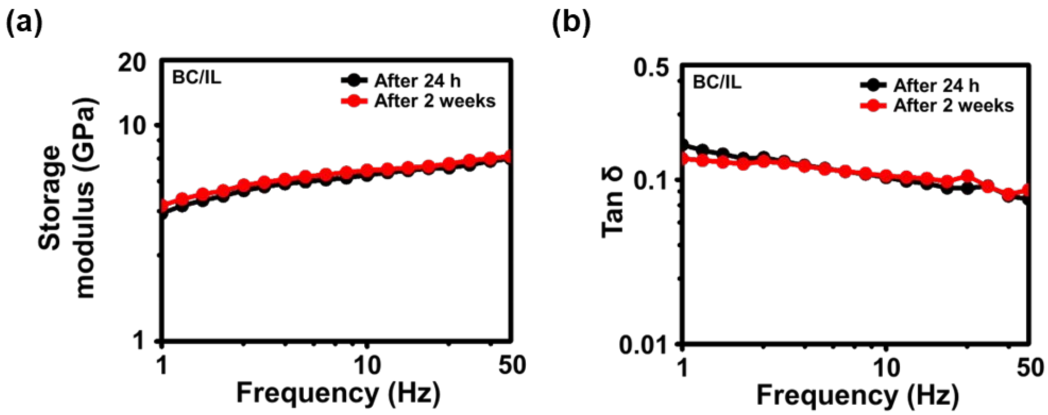


Figure S2. Dynamic mechanical properties of (a) storage modulus and (b) tan δ for BC/IL samples with different immersion times of 24 h and 2 weeks in $EMImBF_4$.

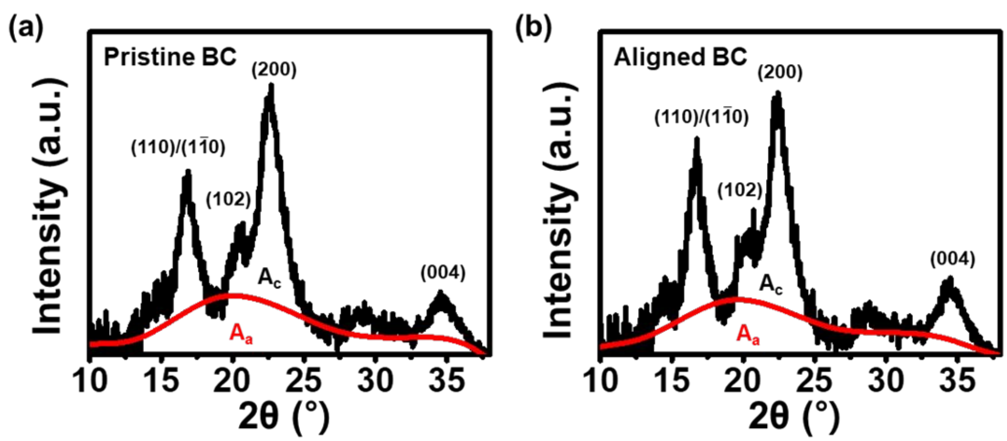


Figure S3. Area of crystalline (A_c) and amorphous (A_a) in WAXS analysis for (a) pristine BC and (b) aligned BC.

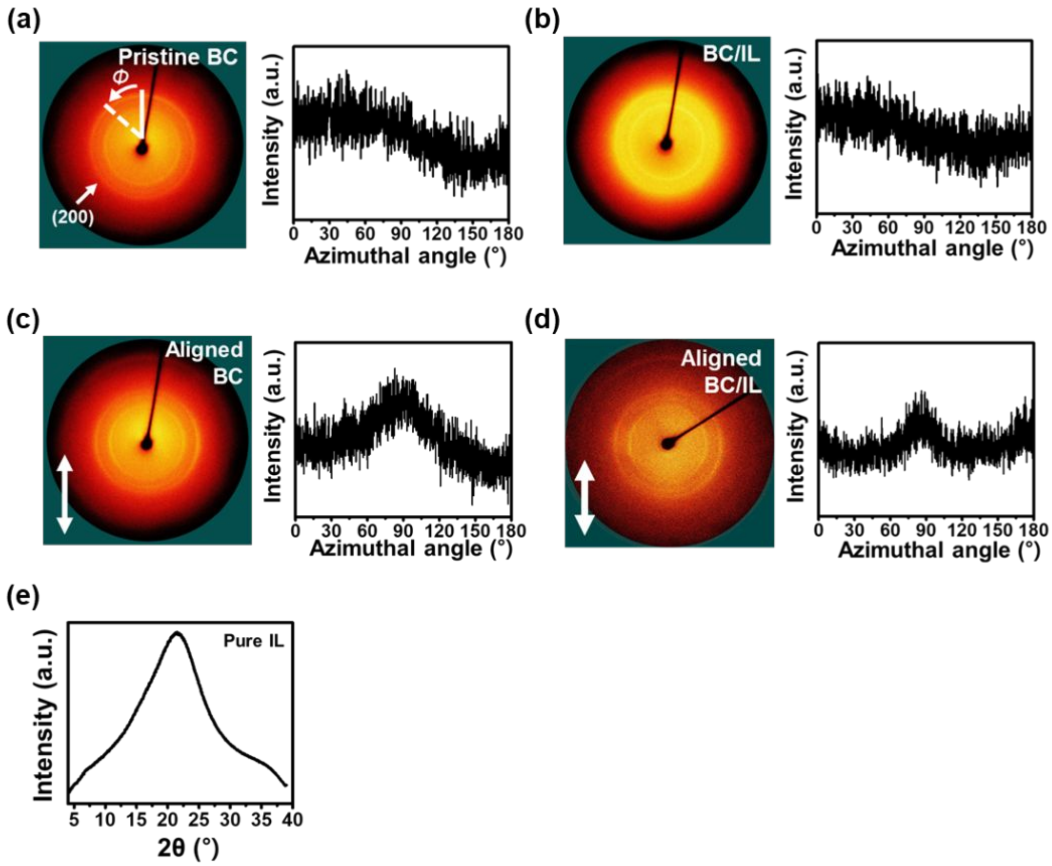


Figure S4. 2D WAXS results of (a) pristine BC, (b) BC/IL, (c) aligned BC, and (d) aligned BC with azimuthal intensity profiles at 2θ = 23°. White arrow in aligned samples indicates stretching direction. (e) Scattering diffractogram of pure IL.

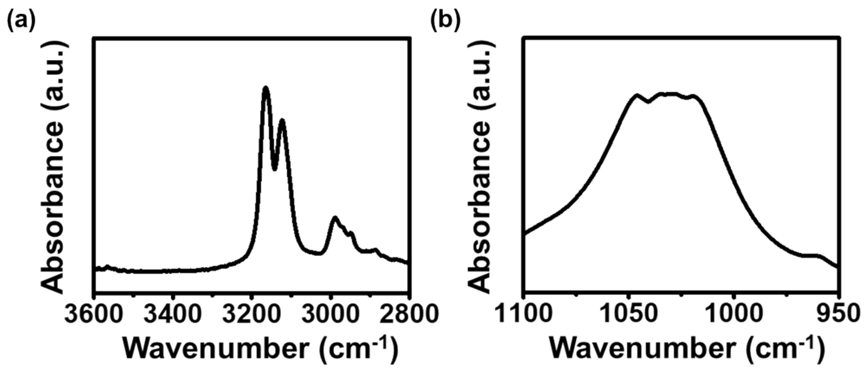


Figure S5. Fourier transform infrared spectroscopy (FT-IR) spectra (a) from 3600 cm^{-1} to 2800 cm^{-1} and (b) from 1100 cm^{-1} to 950 cm^{-1} of pure IL.

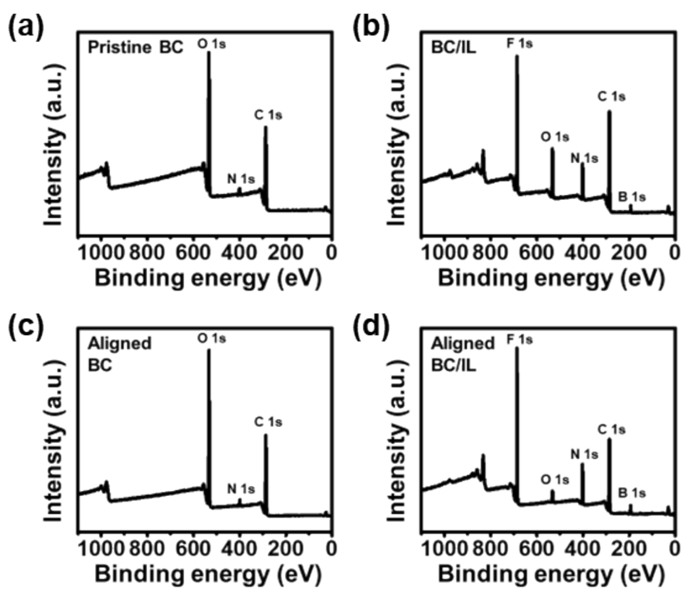


Figure S6. XPS survey spectra profiles of (a) pristine BC, (b) BC/IL, (c) aligned BC, and (d) aligned BC/IL.

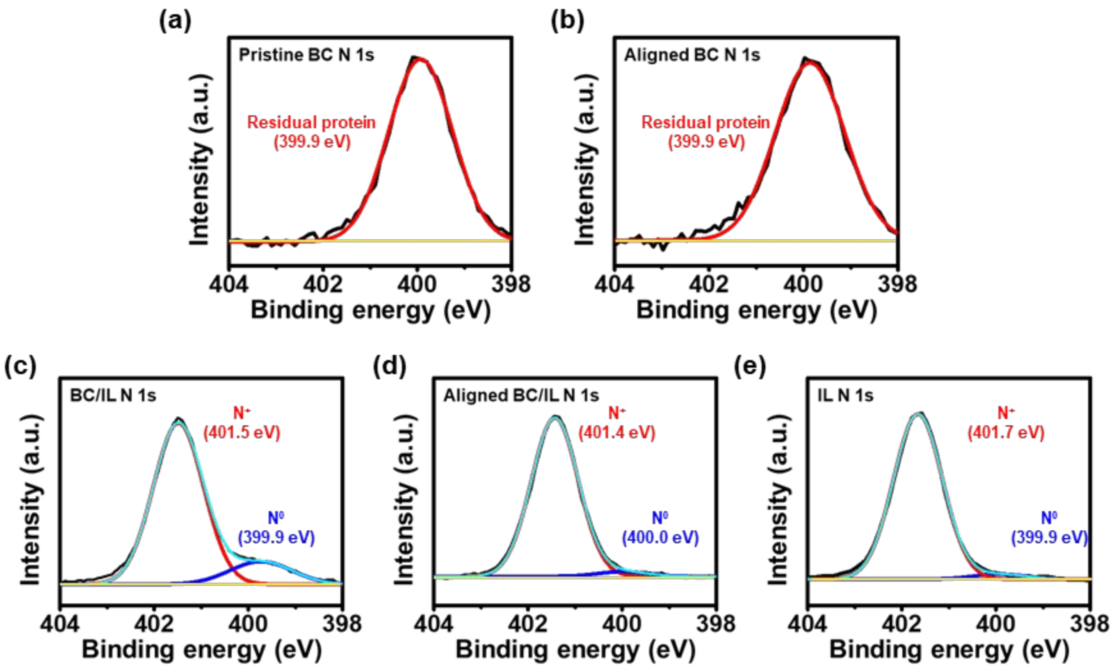


Figure S7. XPS N 1s spectra of (a) pristine BC, (b) aligned BC, (c) BC/IL, (d) aligned BC/IL, and (e) IL samples.

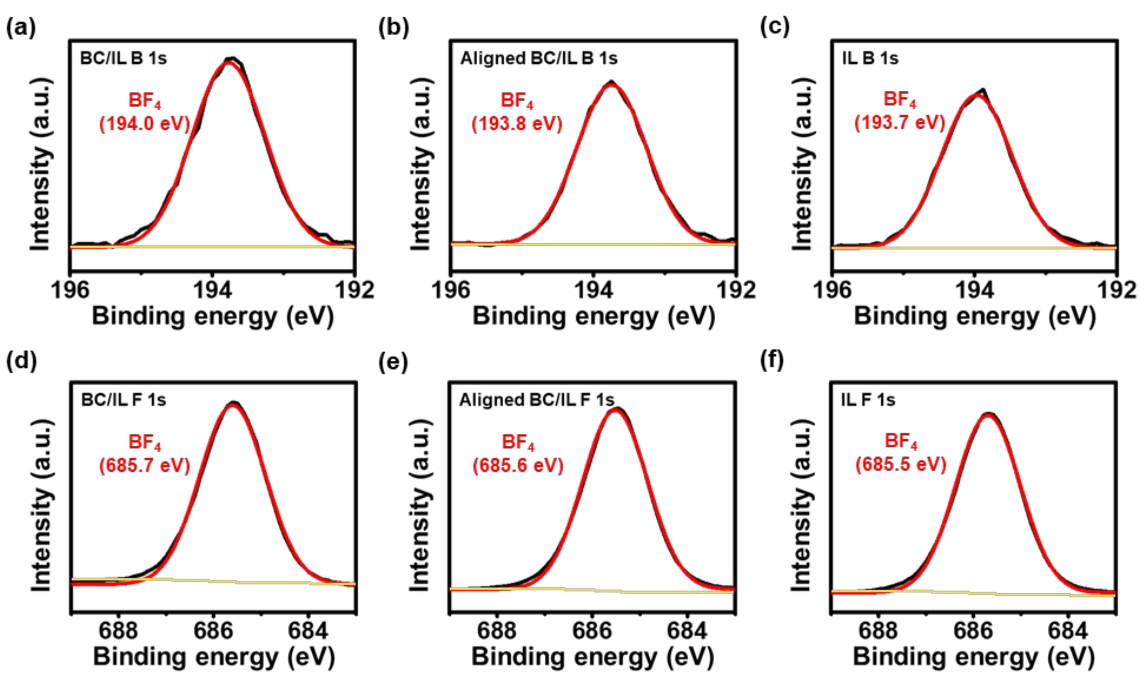


Figure S8. XPS B 1s spectra of (a) IL, (b) BC/IL, and (c) aligned BC/IL and F 1s spectra of (d) IL, (e) BC/IL, and (f) aligned BC/IL.

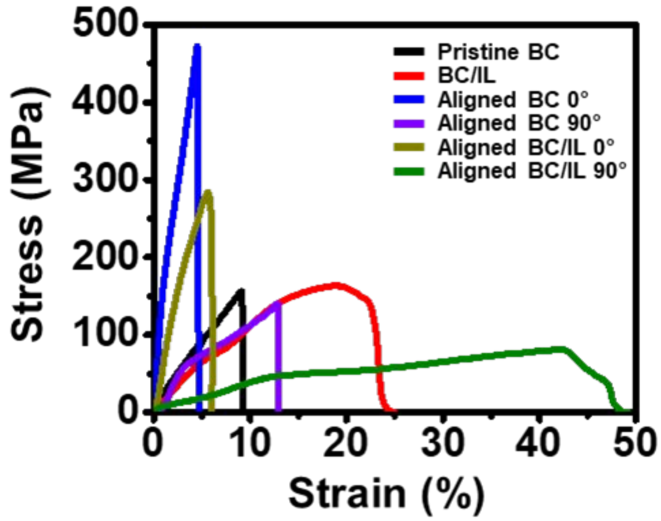


Figure S9. Tensile test results in the parallel and transverse directions with the alignment orientation. Mechanical properties of the aligned BC samples perpendicular to the aligned directions show a decreased modulus of 3.4±0.4 GPa and a lower tensile strength of 142±18 MPa with an increased strain of 12±1.0% in comparison with the values measured in the direction parallel to the aligned direction. Similarly, for aligned BC/IL samples, the elastic modulus and tensile strength decreased to 0.37±0.07 GPa and 74.5±6.1 MPa, respectively, and the elongation increased up to 47 %.

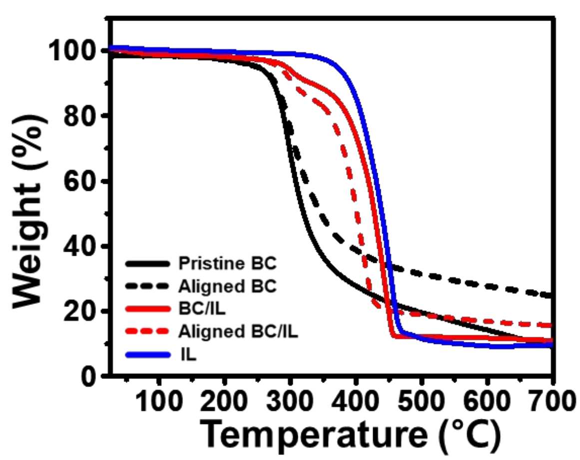


Figure S10. Thermogravimetric analysis (TGA) data of BC samples and pure IL.

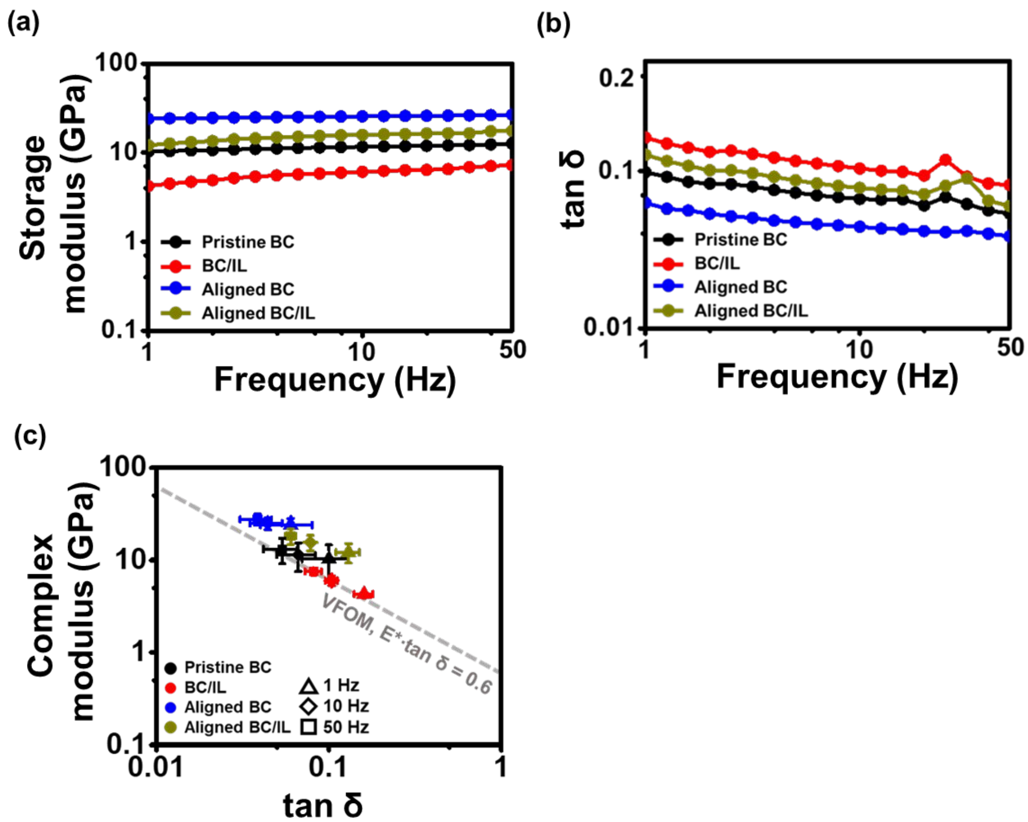


Figure S11. Dynamic mechanical properties of (a) storage modulus, (b) tan δ and (c) complex modulus-tan δ plots for BC and ionogel samples with frequency sweep results at 25 °C.