Supporting Information

Hierarchical Cross-linking for Synergetic Toughening in Crustacean-Mimetic Nanocomposites

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1. Characterization of CNCs

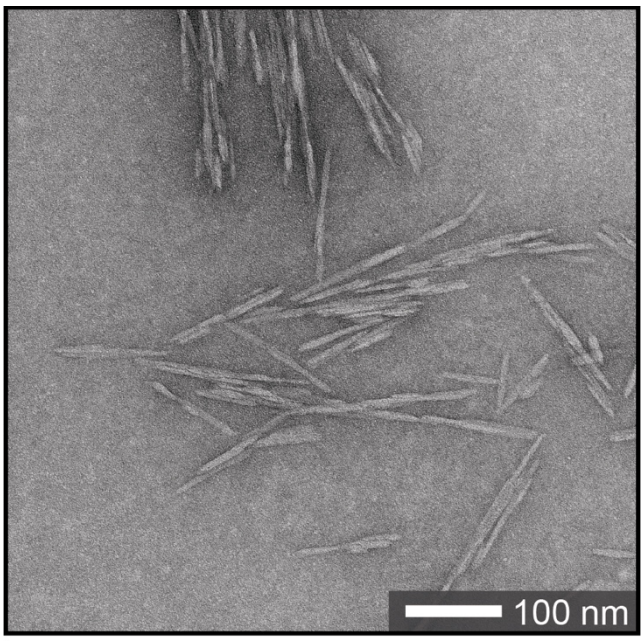

Figure S1. TEM image of CNCs.

2. Characterization of the EG_a-UPy_b copolymers

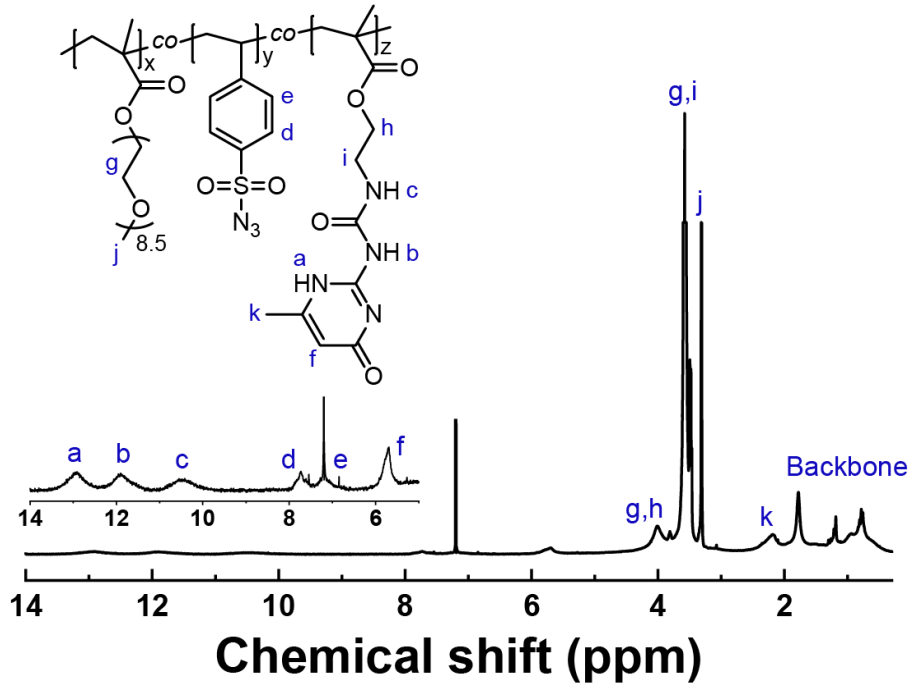

Figure S2. ^{1}H NMR spectrum of EG-SSAz$_5$-UPy$_{10}$ copolymer.

3. Thermal activation of covalent bonds.

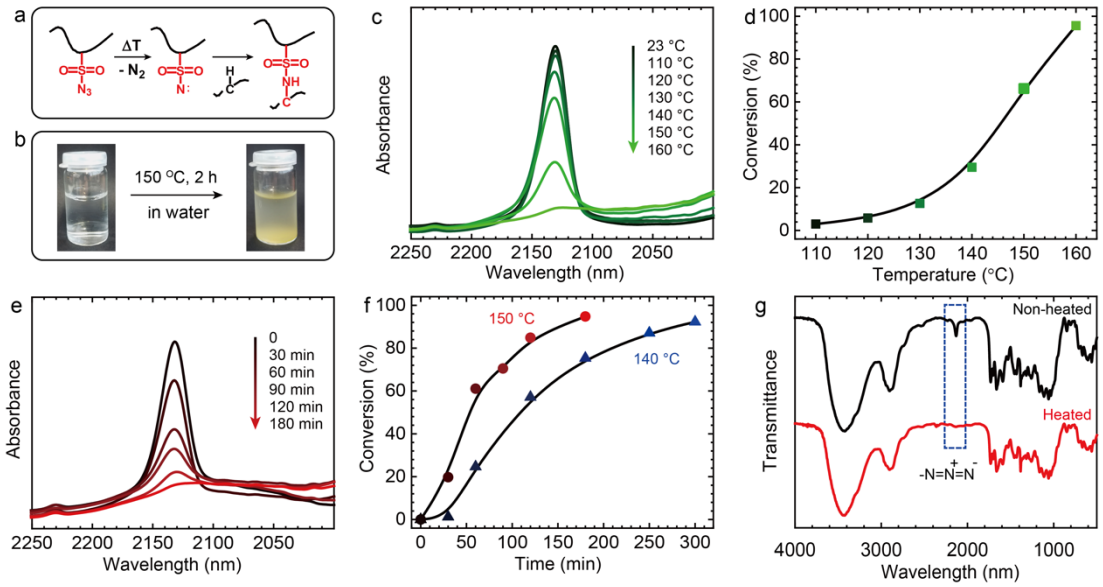

Figure S3. Kinetics of thermal cross-linking employing the activation of SSAz at high temperature to induce covalent bonds. (a) General scheme of the preparation of covalent bonds via heat treatment. (b) The covalent cross-linking leads the change in water-solubility of EG-SSAz$_5$-UPy$_{10}$. (c-f) Cross-linking study of EG-SSAz$_5$-UPy$_{10}$ using FTIR. The peak at 2132 cm^{-1} is attributed to the azide group and strongly diminishes during cross-linking. (c) FTIR spectra of the azide group vibration after heated for 1 h at different temperature. (d) Conversion of azide decomposition as a function of temperature. (e) FTIR spectra of the azide group vibration after heated at 150 °C for different time. (f) Conversion azide decomposition at 150 and 140 °C as a function of time. (g) FTIR spectra of CNC/EG-SSAz$_5$-UPy$_{10}$ = 60/40 nanocomposites.

4. Mechanical tensile properties of CNC/EG-SSAz$_a$-UPy$_b$ nanocomposites

Table S1. Overview of tensile properties of CNC/EG-SSAz$_a$-UPy$_b$ nanocomposites.

Polymer	CNC/polymer (w/w)	E (GPa)	σ_y (MPa)	ε_y (%)	σ_b (MPa)	ε_b (%)	U_t (MJ/m^3)
CNC		12.0 ± 0.2	-	-	71 ± 1	0.8 ± 0.1	0.4 ± 0.1
EG-SSAz$_0$-UPy$_0$	60/40	3.4 ± 0.2	30 ± 3	1.8 ± 0.2	48 ± 1	3.0 ± 0.2	0.9 ± 0.1
EG-SSAz$_5$-UPy$_0$	90/10	9.4 ± 0.9	61 ± 2	1.0 ± 0.1	73 ± 4	1.5 ± 0.3	0.8 ± 0.2
	80/20	6.2 ± 0.3	59 ± 6	1.5 ± 0.2	67 ± 6	2.5 ± 0.3	1.2 ± 0.4
	70/30	4.1 ± 0.3	51 ± 2	2.0 ± 0.2	60 ± 2	3.4 ± 0.5	1.5 ± 0.3
	60/40	3.3 ± 0.3	39 ± 1	2.1 ± 0.1	51 ± 1	4.8 ± 0.2	1.7 ± 0.1
	50/50	2.0 ± 0.2	30 ± 2	2.4 ± 0.1	41 ± 3	5.4 ± 0.4	1.5 ± 0.2
EG-SSAz$_0$-UPy$_{10}$	90/10	9.3 ± 0.3	60 ± 2	0.9 ± 0.1	67 ± 2	1.7 ± 0.2	0.9 ± 0.1
	80/20	7.4 ± 0.4	48 ± 2	1.0 ± 0.1	60 ± 4	3.9 ± 0.7	1.9 ± 0.4
	70/30	5.3 ± 0.5	33 ± 1	0.9 ± 0.1	56 ± 2	6.4 ± 0.7	2.7 ± 0.4
	60/40	4.1 ± 0.3	25 ± 1	0.9 ± 0.1	46 ± 1	7.4 ± 0.4	2.9 ± 0.2
	50/50	2.8 ± 0.2	10 ± 1	0.9 ± 0.2	37 ± 1	8.0 ± 0.7	2.1 ± 0.1
EG-SSAz$_5$-UPy$_{10}$	90/10	10.5 ± 0.9	75 ± 2	1.1 ± 0.1	88 ± 3	2.4 ± 0.5	1.6 ± 0.3
	80/20	8.1 ± 0.9	56 ± 1	1.1 ± 0.1	74 ± 1	5.1 ± 0.1	3.1 ± 0.1
	70/30	5.8 ± 0.2	34 ± 2	1.0 ± 0.4	65 ± 2	7.5 ± 0.6	3.7 ± 0.3
	60/40	4.9 ± 0.4	28 ± 2	1.0 ± 0.1	61 ± 1	7.8 ± 0.6	3.6 ± 0.3
	50/50	3.2 ± 0.2	20 ± 1	0.9 ± 0.1	49 ± 2	8.3 ± 0.7	2.8 ± 0.2
EG-SSAz$_{15}$-UPy$_0$	70/30	6.4 ± 0.3	57 ± 5	1.4 ± 0.1	66 ± 4	2.5 ± 0.4	1.2 ± 0.1
	60/40	3.8 ± 0.3	47 ± 1	2.1 ± 0.1	60 ± 1	4.8 ± 0.5	2.1 ± 0.3
EG-SSAz$_0$-UPy$_{30}$	70/30	7.2 ± 0.3	50 ± 1	1.2 ± 0.1	68 ± 1	5.1 ± 0.4	2.7 ± 0.2
	60/40	5.5 ± 0.5	36 ± 1	1.0 ± 0.1	61 ± 2	5.8 ± 1.1	2.6 ± 0.6
EG-SSAz$_5$-UPy$_{30}$	70/30	7.6 ± 0.2	51 ± 3	1.0 ± 0.1	79 ± 2	5.3 ± 0.6	3.2 ± 0.4
	60/40	6.4 ± 0.5	47 ± 1	1.1 ± 0.1	77 ± 1	6.3 ± 0.7	3.6 ± 0.5
EG-SSAz$_{15}$-UPy$_{10}$	70/30	6.6 ± 0.3	41 ± 1	0.9 ± 0.1	73 ± 1	6.1 ± 0.9	3.3 ± 0.5
	60/40	6.4 ± 0.5	32 ± 1	0.8 ± 0.1	70 ± 1	6.5 ± 0.2	3.2 ± 0.2
EG-SSAz$_{15}$-UPy$_{30}$	70/30	10.7 ± 0.9	63 ± 3	0.9 ± 0.1	88 ± 3	3.9 ± 0.3	2.8 ± 0.2
	60/40	9.5 ± 0.3	59 ± 1	1.0 ± 0.1	82 ± 1	4.3 ± 0.1	2.9 ± 0.2

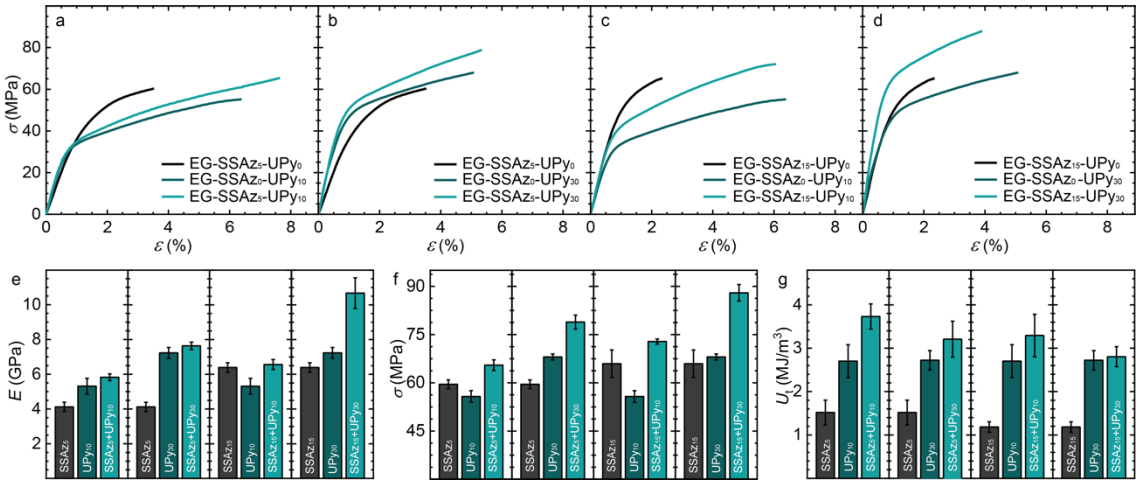

Figure S4. Synergistic toughening in CNC/EG-SSAz$_a$-UPy$_b$ = 70/30 nanocomposites. Tensile curves for the nanocomposites with hierarchical cross-linking: (a) CNC/EG-SSAz$_5$-UPy$_{10}$, (b) CNC/EG-SSAz$_5$-UPy$_{30}$, (c) CNC/EG-SSAz$_{15}$-UPy$_{10}$ and (d) CNC/EG-SSAz$_{15}$-UPy$_{30}$. The nanocomposites with corresponding single interaction are shown as references. Comparison of (e) E, (f) σ_b, and (g) ε_b extracted from tensile curves.

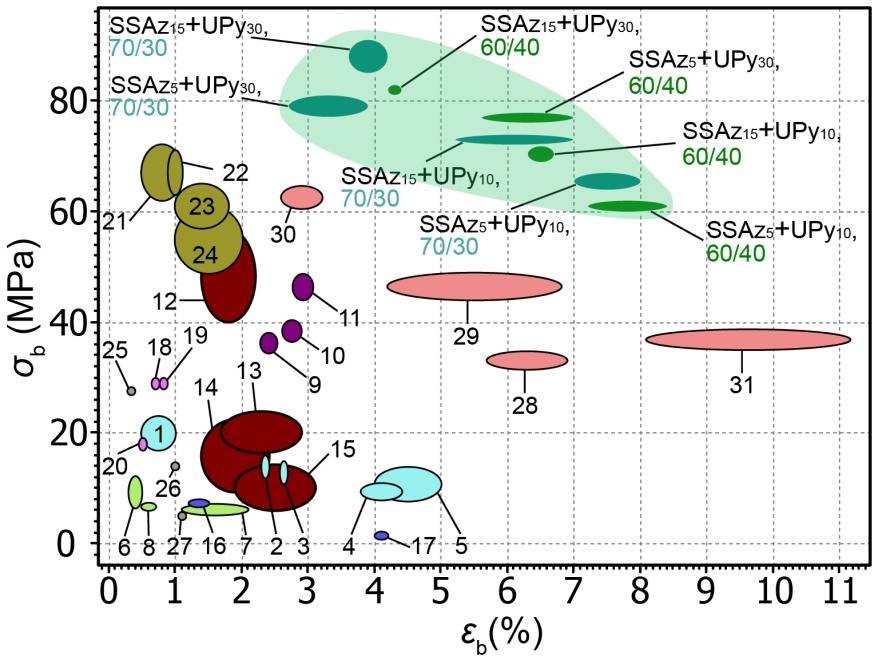

Figure S5. Comparison of mechanical properties to state-of-the-art chiral nematic CNCs nanocomposites. Comparison of the strength with elongation at break for CNCs nanocomposites in Ashby plots.