Supporting Information

A Bio-inspired Approach to Engineering Water-Responsive, Mechanically-Adaptive Materials

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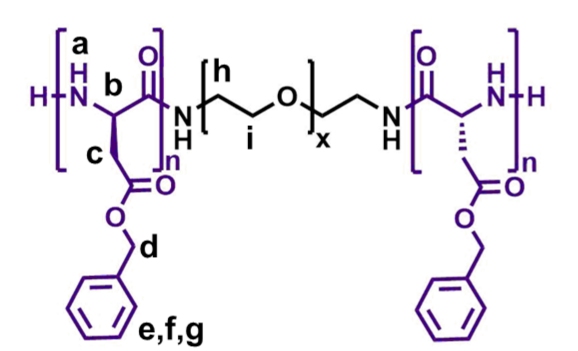
Abbreviations and nomenclature

^{1}H nuclear magnetic resonance (^{1}H NMR)
Poly(β-benzyl-L-aspartate) (PBLA)
α,ω-Bis(amine)poly(ethylene glycol) (PEG)
Degree of polymerization (DP)
1,6-hexamethylene diisocyanate (HDI)
Polyurea (PU)
Peptide-polyurea hybrids (PPUs)
Cellulose nanocrystals (CNCs)
Gel permeation chromatography (GPC)
Atomic force microscopy (AFM)
Poly(methyl methacrylate) (PMMA)
Nanocellulose (NC)

The following nomenclature was utilized. An-X and An-X/CNCY were used for the PPUs and the PPU/CNC nanocomposites, respectively, where A indicates non-chain extended peptide-polyurea hybrids consisting of PBLA-*b*-PEG-*b*-PBLA as the soft segment, n is the peptide repeat length (21), X is the peptide weight fraction in the resultant sample (20 or 40 wt%), and Y is CNC content (wt%). The control film without PBLA was denoted by PEG-HDI PU.



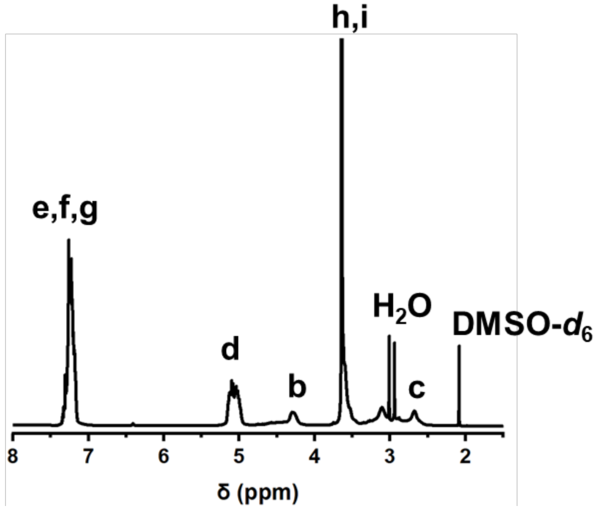
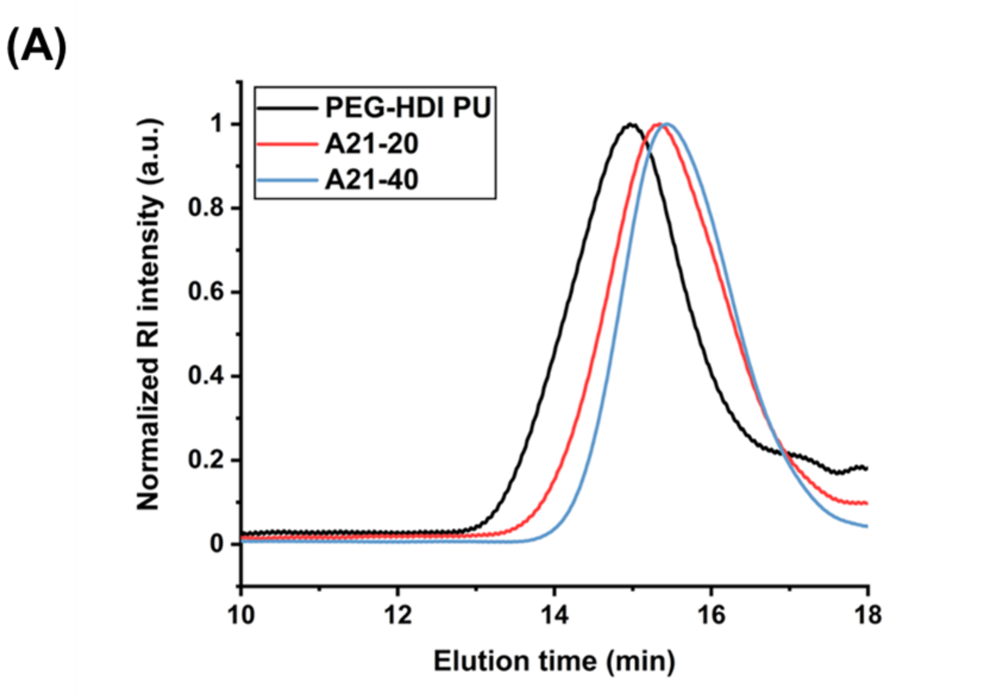


Figure S1. [1]H NMR spectrum of PBLA-*b*-PEG-*b*-PBLA triblock recorded in dimethyl sulfoxide (DMSO)-d_6. The PBLA repeat length or the degree of polymerization of the PBLA block (n) was determined from the integration ratio of resonance corresponding to PEG block at δ 3.9 ppm and PBLA block at δ ~ 5.5 ppm. The peak at δ 3.9 ppm corresponding to the PEG backbone was used as a reference peak, with the integration value of this peak set to 188 (x=47), as identified from end group analysis of the PEG homopolymer (~ 2,000 g/mol). The relative DP ratio of PEG(x)/PBLA(n) is ~2, indicating that the PEG block has approximately double the repeat units compared to the PBLA block in the resulting triblock copolymer.



(B)

	PBLA[a] (wt%)	M_n[b] (kg mol^{-1})	$Đ$[b]
PEG-HDI PU	0	118.6	3.0
A21-20	20	57.0	2.9
A21-40	40	48.6	2.5

[a] Determined from Equation S1.
[b] Calculated from GPC using DMAc/0.5 wt% of LiBr as the eluent and PMMA as standards.

Figure S2. (A) GPC traces for the synthesized PEG-HDI PU (control) and PPUs (A21-20 and A21-40) **(B)** Table summarizing the PBLA weight fraction, number-average molecular weight (M_n) and dispersity ($Đ$) of the synthesized control and PPUs.

Equation S1. PBLA content for PPU samples

$$\mathrm{wt\%\ (PBLA)} = 100 \times \left(\frac{\mathrm{xM_{PBLA}}}{\mathrm{xM_{PBLA}} + \mathrm{yM_{PEG}} + \mathrm{zM_{HDI}}}\right)$$

where x, y and z are the molar quantities of the PBLA, PEG, and HDI, respectively, and M_{PBLA}, M_{PEG} and M_{HDI} are the molecular weights of PBLA, PEG and HDI, respectively.

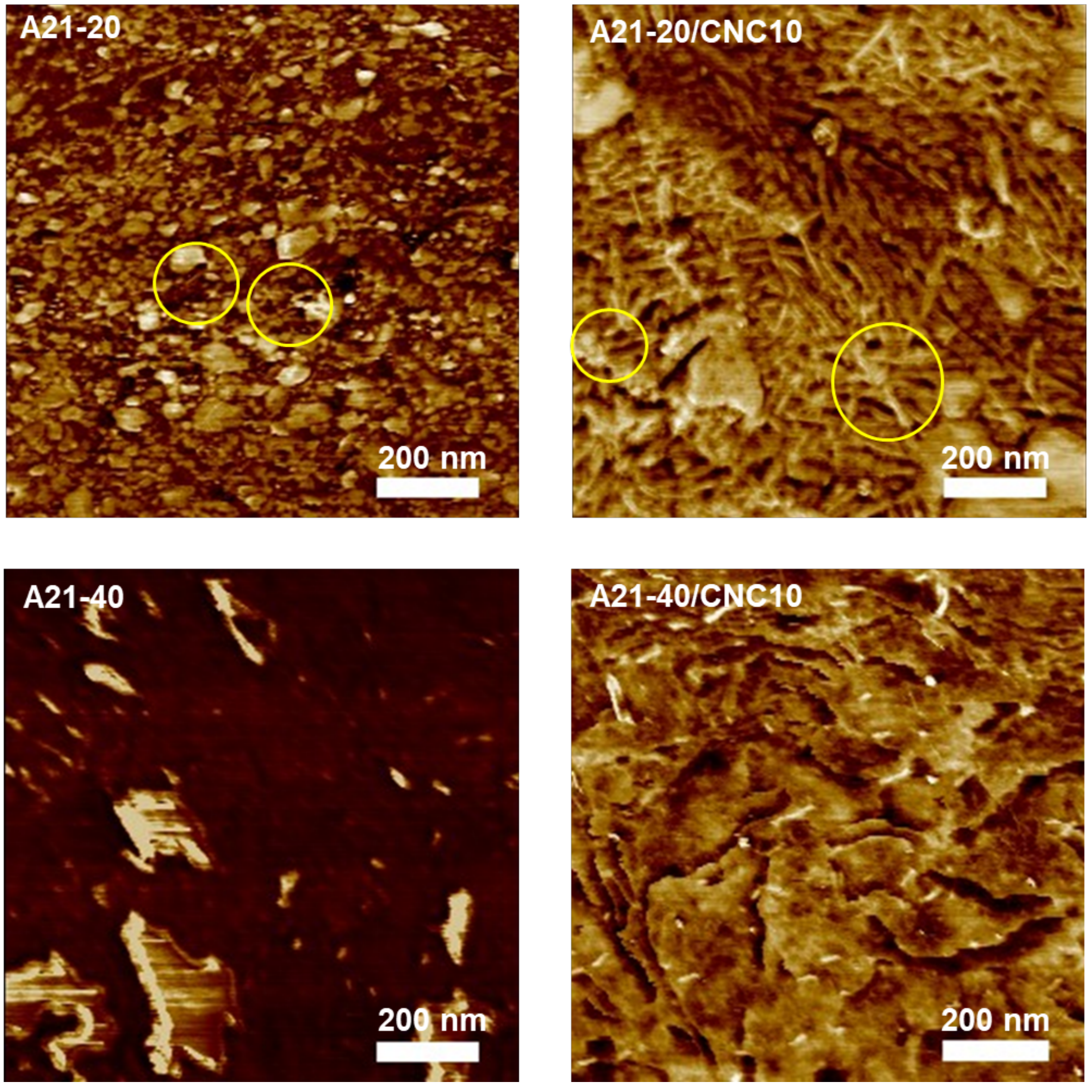


Figure S3. Magnified AFM phase images of the surface of dried PPU and PPU/CNC nanocomposite films (1 x1 μm). Yellow circles indicate the interconnected rods.

Mathematical model to predict Young's modulus

The **Halpin-Tsai Model**[1] is used to predict the mechanical properties of composites containing randomly oriented nanofibers. This model excludes filler-filler interactions, assuming that fillers are dispersed homogeneously in a polymer matrix *via* *i*deal filler-matrix interactions. The extent of reinforcement is determined by the following factors: 1) individual mechanical properties of the pristine matrix and the filler material, 2) the filler aspect ratio, 3) the degree of filler alignment, and 4) the filler volume fraction.

$$E_{c,L} = \frac{E_m(1 + 2\frac{L}{D}\eta_L\varphi_f)}{(1 - \eta_L\varphi_f)}, \eta_L = \frac{E_f - E_m}{E_f + 2\frac{L}{D}E_m}$$

$$E_{c,T} = \frac{E_m(1 + 2\eta_T\varphi_f)}{(1 - \eta_T\varphi_f)}, \eta_T = \frac{E_f - E_m}{E_f + 2E_m}$$

$$E_{c,R} = aE_{c,L} + (1 - a)E_{c,T}$$

$$a = 0.13 + 0.0815\varphi_f - 1.669\frac{E_m}{E_f}$$

Where E indicates Young's modulus: E_L is longitudinal modulus E_c transverse modulus, and E_R is the modulus of a randomly oriented composite. The subscripts m, f, and c are assigned to the matrix, filler, and composite, respectively. L/D is the filler aspect ratio (*i.e.,* the ratio of the longest dimension (length) to the shortest dimension (diameter)). a is defined as the weight fraction. φ_f is the volume fraction of the filler.

The **Percolation model**[2-3] describes systems exhibiting strong filler-filler interactions, yielding a rigid network above a critical filler fraction (*i.e.,* percolation threshold). Above the percolation threshold (φ_t), the modulus of the composite (E_c) is mostly determined by the rigidity of the filler network (E_f).

$$E_c = \frac{(1 - 2\Psi + \Psi\varphi_f)E_mE_f + (1 - \varphi_f)\Psi E_f^2}{(1 - \varphi_f)E_f + (\varphi_f - \Psi)E_m}$$

$$f(x) = \begin{cases} 0 \quad , & \varphi_f \leq \varphi_t \\ \varphi_f(\frac{\varphi_f - \varphi_t}{1 - \varphi_t})^{0.4}, & \varphi_f > \varphi_t \end{cases}$$

For simplicity, it is assumed that the filler distribution is isotropic, and the aspect ratio is fixed to calculate φ_t using the equation below.

$$\varphi_t = \frac{\frac{2L}{D} + \frac{4}{3}}{\frac{32}{3}\left[1 + \frac{3}{2}\left(\frac{L}{D}\right) + \frac{3}{8}\left(\frac{L}{D}\right)^2\right]}$$

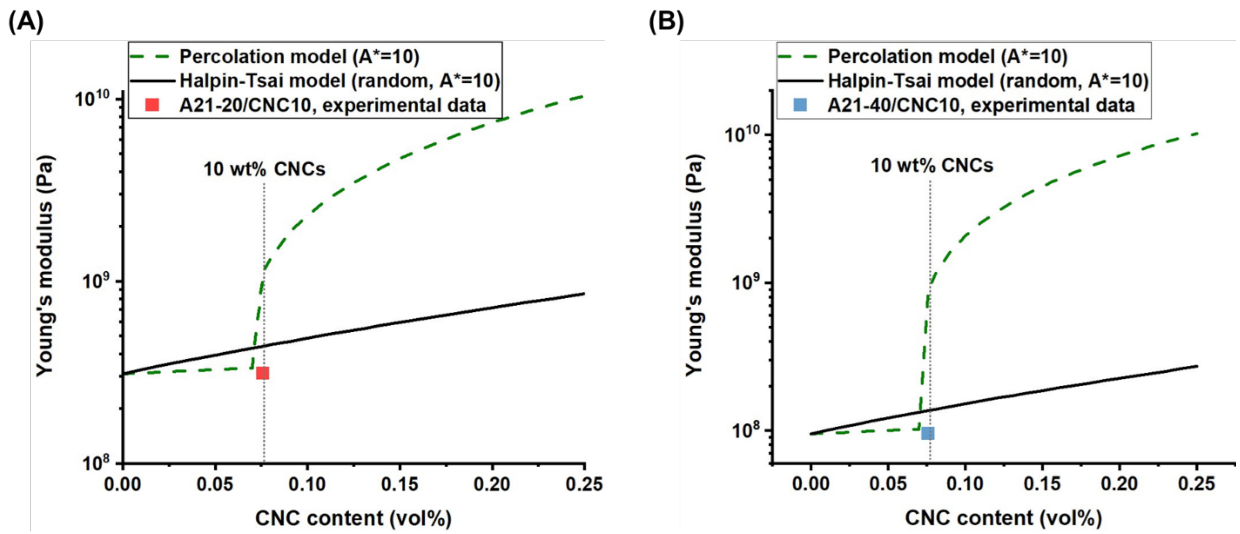


Figure S4. Experimental Young's modulus of **(A)** A21-20/CNC10 and **(B)** A21-40/CNC10 nanocomposites compared with the percolation model (green dash curve) and the Halpin-Tsai model for randomly-oriented CNCs (black solid line). Based on the supplier's information on CNCs, the aspect ratio (A*) was set to 10 for model fitting.

Table S1. Swelling behavior of PPUs as a function of PBLA and CNC content.

Sample	**PBLA content (%)**	**CNC content (wt%)**	**Swelling ratio (%)**
PEG-HDI PU	0	0	N/A (dissolved)
A21-20	20	0	780
A21-40	40	0	195
A21-20/CNC10	20	10	1080
A21-40/CNC10	40	10	380

Table S2. List of the values for the extent of water-responsive stiffness change ($\Delta E = E'_{dry} - E'_{wet}$) for various polymer/cellulose nanocomposites (from the literature and from this study) with 10 wt% of nanocellulose (NC). These values were used to plot **Figure 6C**.

Matrix type	**Nanocellulose content (wt%)**	**E'_{dry} of matrix (MPa)**	**Average ΔE of matrix (MPa)**	**E'_{dry} of polymer/cellulose nanocomposite (MPa)**	**Average ΔE of polymer/cellulose nanocomposite (MPa)**	**Nomenclature for nanocomposite**	**Ref.**
Natural rubber (NR)	10	1	0	1.8	0.2	NR/NC10	[4]
Epoxidized natural (ENR)	10	1.5	0	10	8	ENR/NC10	[4]
Poly(styrene-*co*-butadiene) (SBR)	10	1	0	73	61	SBR/NC10	[5]
Polybutadiene (PBD)	10	0.5	0	94	72	PBD/NC10	[5]
Polyether-based polyurethane (PU)	10	16	-	125	78	PU/NC10	[6]
Thermoplastic polyurethane (TPU)	10	12	0	200	50	TPU/NC10	[7]
Peptide-polyurea	0			212	210	A21-20	Our work
Peptide-polyurea	0			88	73	A21-40	Our work
Peptide-polyurea	10	212	210	385	397	A21-20/CNC10	Our work
Peptide-polyurea	10	88	73	360	334	A21-40/CNC10	Our work

References

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