Supplementary Information

Optimization of spray-coated nanochitin/nanocellulose films as renewable oxygen barrier layers via thermal treatment

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Table S1. Properties of cellulose acetate substrate.

Degree of substitution	2.1-2.4 [a]
Degree of polymerization	145-190 [a]
Thickness (μm)	76 ± 1
Density (g/cm^3)	1.23 ± 0.10 [b]

[a] Data available in Ref 1.
[b] Density was measured by displacement (ASTM D792) in triplicate by using isopropyl alcohol.

Table S2. Properties of chitin nanowhisker suspension.

Concentration (wt %)	0.5
Length (nm)	112 ± 53
Width (nm)	4.4 ± 0.9
Degree of acetylation (%)	62.4 ± 4.8
Viscosity @ 300 s^{-1} (cP)	5.3

Table S3. Properties of cellulose nanocrystal suspension.

Concentration (wt %)	0.5
Length (nm)	134 ± 41
Width (nm)	6.0 ± 2.6
Sulfur content (mmol/g-dry-CNC)	1.06
Viscosity @ 300 s^{-1} (cP)	1.3

Characterizations of chitin nanowhisker and cellulose nanocrystal suspensions

Dimensions of ChNWs and CNCs were measured by atomic force microscopy (AFM; Dimension XR, Bruker, UK) at 0.990 Hz.[2] The suspensions were diluted to 0.001 wt% by adding pH 3 HOAc solution (for ChNW) or deionized water (for CNC), cast on silicon wafer, dried at 70 ℃, and conditioned under room atmosphere overnight before characterization. At least 100 nanowhiskers or nanocrystals were selected randomly to obtain the size distribution.

The degree of acetylation of ChNW was characterized by potentiometric titration as previously reported.[2] Briefly, ChNW suspension was treated with anion exchange resin (Amberlite IRN-78, Alfa Aesar, USA), washed with water, acidified with hydrochloric acid solution, and titrated against NaOH solution.

The viscosities of 0.5 wt% ChNW and 0.5 wt% CNC were characterized using a rheometer (MCR 302, Anton Paar, USA) at 23 °C using a cone-plate geometry.[3] The cone had a diameter of 50 mm, cone angle of 1.01°, and truncation of 0.053 mm, and the bottom plate insert was 60 mm in diameter.

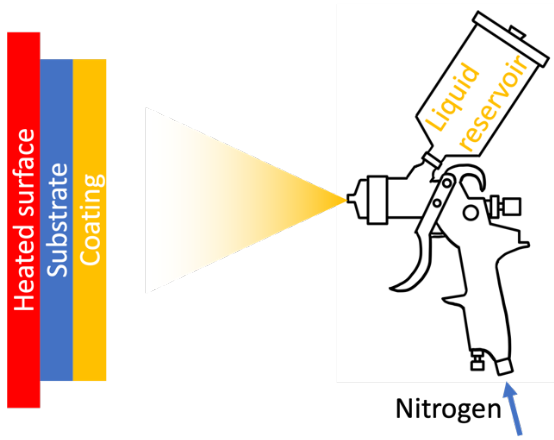

Figure S1. Schematic of the spray coating setup.

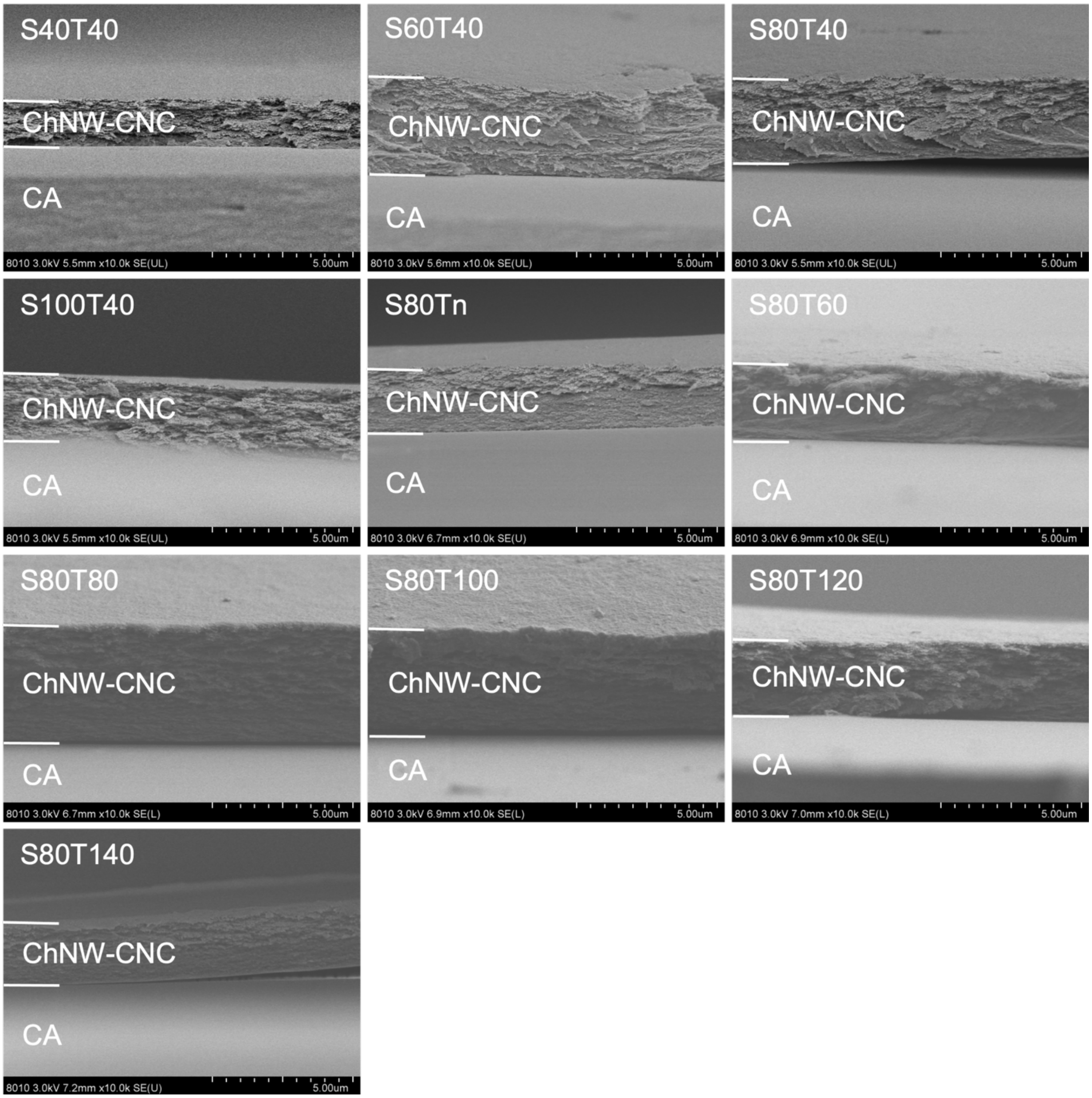

Figure S2. Cross-sectional SEM images for ChNW-CNC coatings with an exposed CA top surface.

Table S4. Oxygen permeabilities of CA films treated under different conditions.

Sample	Oxygen permeability ($cm^3 \cdot \mu m/m^2/day/kPa$)
CAS40	526 ± 10
CAS60	498 ± 7
CAS80	496 ± 7
CAS100	504 ± 8
CAT40	557 ± 8
CAT60	606 ± 9
CAT80	499 ± 7
CAT100	584 ± 16
CAT120	533 ± 7
CAT140	546 ± 8

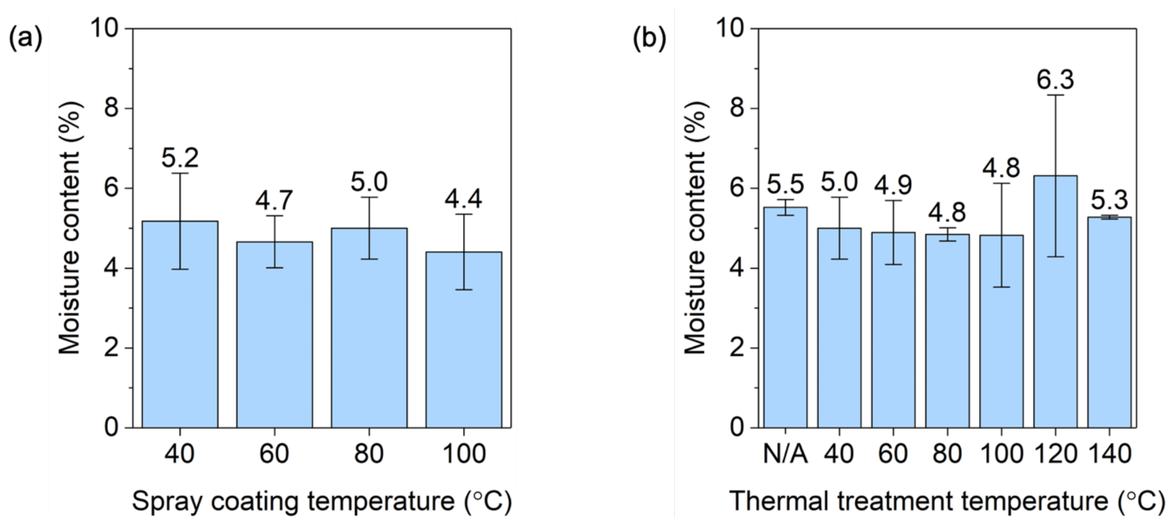

Figure S3. Moisture content of ChNW-CNC coating for films prepared at different spray coating temperatures (a) and thermal treatment temperatures (b) determined by TGA. 'N/A' represents sample S80Tn without being thermally treated.

Table S5. Oxygen and water vapor properties of common plastics for food packaging applications versus the coated film S80T140.

Film	Oxygen permeability [a] ($cm^3·µm/m^2$/day/kPa)	Water vapor transmission rate [b] ($g·µm/m^2$/day)
PE[4]	500-2000	0.5-2
PS[4]	1000-1500	1-4
PP[4]	500-1000	0.2-0.4
PVC[4]	20-80	1-2
PLA[5,6]	70-1300	2.2
PET[4]	10-50	0.5-2
CA	535 ± 38	8.3 ± 0.1
S80T140	11.5 ± 0.9	6600 ± 100

[a] The oxygen permeability values were all obtained at 23 ℃ and 50% RH.
[b] The water vapor transmission rate values for PE, PS, PP, PVC, and PET were obtained at 23 ℃ and 85% RH, while the values for PLA, CA, and S80T140 were obtained at 23 ℃ and 50% RH.

Table S6. Densities of selected coated CA films before and after six months of conditioning at room temperature and ~53% RH.

Sample	Density (g/cm^3)	
	Before	After
S40T40	1.13 ± 0.07	1.20 ± 0.04
S80T140	1.13 ± 0.07	1.26 ± 0.08

Table S7. Water contact angle on untreated CA and coated films.

	Water contact angle (°)
CA	65.0 ± 1.5
S40T40	49.8 ± 4.5
S60T40	42.2 ± 4.5
S80T40	40.2 ± 4.1
S100T40	42.1 ± 0.9
S80Tn	38.8 ± 2.8
S80T60	37.5 ± 1.8
S80T80	38.7 ± 2.4
S80T100	38.0 ± 0.7
S80T120	45.3 ± 6.2
S80T140	44.1 ± 4.2

The water contact angle (WCA) on the untreated CA film was significantly higher than those on the CNC sides of the coated films because the CNC was more hydrophilic than CA. The WCA on S40T40 was slightly higher than those on the other coated samples, which is likely the result of its highest surface roughness. Generally, no statistically significant difference in WCA was observed among the other coated samples.

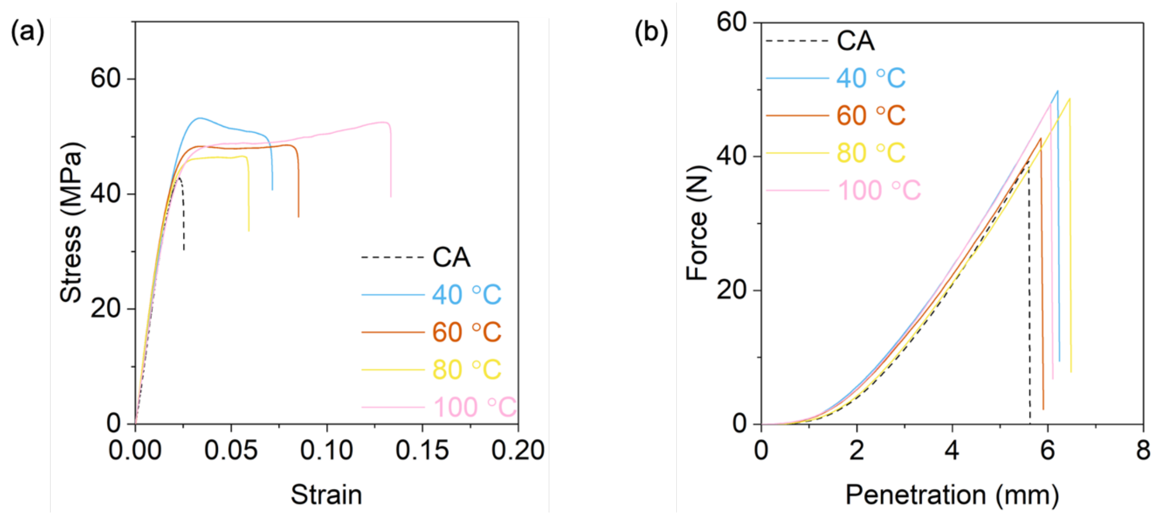

Figure S4. Selected stress-strain curves (a) and force-penetration (b) for untreated CA and coated CA films with different spray coating temperatures.

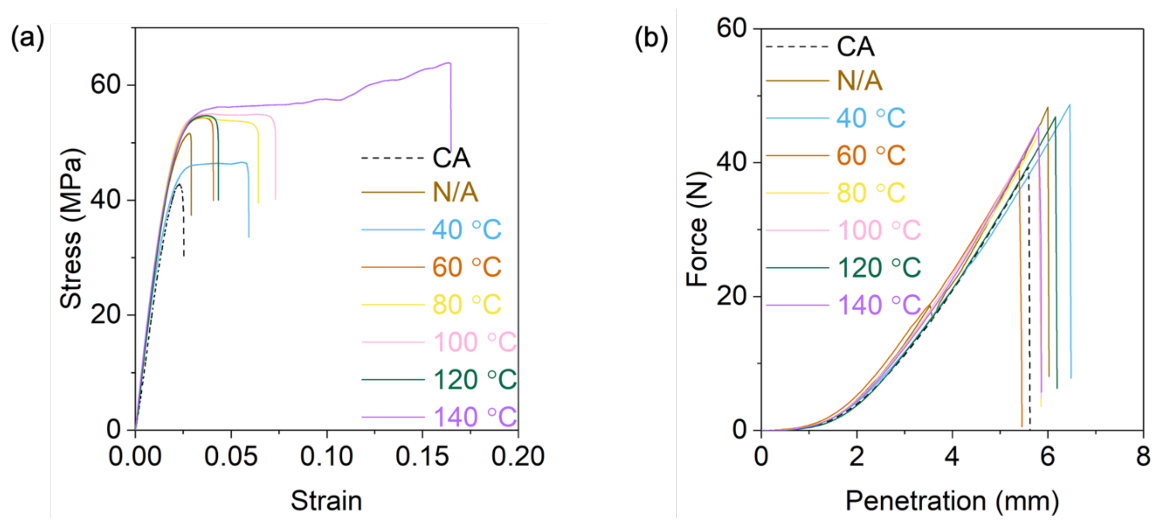

Figure S5. Selected stress-strain curves (a) and force-penetration (b) for untreated CA and coated CA films with different thermal treatment temperatures.

Table S8. Two tailed P-values for mean breaking force. Values in red indicate the difference in means between the two samples being compared is significant (α = 0.05).

P-value	CA	S40 T40	S60 T40	S80 T40	S100 T40	S80 Tn	S80 T60	S80 T80	S80 T100	S80 T120	S80 T140
CA	1.00										
S40T40	0.01	1.00									
S60T40	0.03	0.30	1.00								
S80T40	0.001	0.88	0.37	1.00							
S100T40	0.09	0.57	0.88	0.64	1.00						
S80Tn	0.0004	0.93	0.31	0.94	0.60	1.00					
S80T60	0.14	0.03	0.11	0.02	0.21	0.02	1.00				
S80T80	0.01	0.06	0.40	0.06	0.50	0.03	0.21	1.00			
S80T100	0.004	0.13	0.79	0.17	0.74	0.09	0.10	0.35	1.00		
S80T120	0.004	0.98	0.27	0.85	0.56	0.90	0.02	0.03	0.09	1.00	
S80T140	0.02	0.30	0.89	0.39	0.94	0.31	0.08	0.27	0.63	0.26	1.00
CAS40	0.001	0.03									
CAS60	0.003		0.08								
CAS80	0.004			0.004		0.01	0.54	0.045	0.03	0.02	0.048
CAS100	0.001				0.23						
CAT40	0.051	0.02	0.11	0.01	0.22						
CAT60	0.70						0.54				
CAT80	0.03							0.11			
CAT100	0.001								0.03		
CAT120	0.04									0.01	
CAT140	0.02										0.04

Table S8. (continued)

P-value	CA S40	CA S60	CA S80	CA S100	CA T40	CA T60	CA T80	CA T100	CA T120	CA T140
CAS40	1.00									
CAS60	0.005	1.00								
CAS80	0.003	0.24	1.00							
CAS100	0.42	0.08	0.06	1.00						
CAT40	0.16	0.48	0.62	0.09	1.00					
CAT60	0.54	0.70	0.73	0.48	0.82	1.00				
CAT80	0.72	0.32	0.27	1.00	0.20	0.49	1.00			
CAT100	0.68	0.13	0.09	0.78	0.12	0.51	0.88	1.00		
CAT120	0.61	0.70	0.58	0.41	0.43	0.63	0.52	0.51	1.00	
CAT140	0.29	0.99	0.81	0.17	0.57	0.70	0.34	0.24	0.74	1.00

Table S9. Two tailed P-values for mean modulus. Values in red indicate the difference in means between the two samples being compared is significant (α = 0.05).

P-value	CA	S40 T40	S60 T40	S80 T40	S100 T40	S80 Tn	S80 T60	S80 T80	S80 T100	S80 T120	S80 T140
CA	1.00										
S40T40	0.77	1.00									
S60T40	0.19	0.39	1.00								
S80T40	0.13	0.27	0.67	1.00							
S100T40	0.82	0.91	0.17	0.10	1.00						
S80Tn	0.01	0.04	0.01	0.02	0.004	1.00					
S80T60	0.02	0.06	0.03	0.0497	0.01	0.30	1.00				
S80T80	0.01	0.052	0.02	0.052	0.01	0.46	0.84	1.00			
S80T100	0.02	0.07	0.04	0.10	0.01	0.17	0.49	0.49	1.00		
S80T120	0.048	0.13	0.22	0.43	0.03	0.10	0.23	0.22	0.39	1.00	
S80T140	0.07	0.14	0.30	0.47	0.07	0.30	0.52	0.48	0.68	0.88	1.00
CAS40	0.02	0.06									
CAS60	0.02		0.06								
CAS80	0.06			0.52		0.04	0.10	0.10	0.19	0.81	0.74
CAS100	0.11				0.08						
CAT40	0.05	0.08	0.09	0.20	0.02						
CAT60	0.02						0.34				
CAT80	0.03							0.16			
CAT100	0.03								0.80		
CAT120	0.11									0.28	
CAT140	0.04										0.93

Table S9. (continued)

P-value	CA S40	CA S60	CA S80	CA S100	CA T40	CA T60	CA T80	CA T100	CA T120	CA T140
CAS40	1.00									
CAS60	0.73	1.00								
CAS80	0.10	0.26	1.00							
CAS100	0.0002	0.06	0.29	1.00						
CAT40	0.04	0.27	0.83	0.08	1.00					
CAT60	0.33	0.86	0.22	0.01	0.14	1.00				
CAT80	0.04	0.51	0.40	0.00	0.34	0.38	1.00			
CAT100	0.53	0.79	0.40	0.11	0.44	0.88	0.77	1.00		
CAT120	0.0003	0.06	0.29	0.999	0.08	0.01	0.003	0.11	1.00	
CAT140	0.15	0.41	0.68	0.13	0.78	0.37	0.68	0.60	0.13	1.00

Table S10. Two tailed P-values for mean yield stress. Values in red indicate the difference in means between the two samples being compared is significant (α = 0.05).

P-value	CA	S40 T40	S60 T40	S80 T40	S100 T40	S80 Tn	S80 T60	S80 T80	S80 T100	S80 T120	S80 T140
CA	1.00										
S40T40	0.10	1.00									
S60T40	0.14	0.55	1.00								
S80T40	0.055	0.78	0.26	1.00							
S100T40	0.04	0.58	0.06	0.76	1.00						
S80Tn	0.01	0.046	0.03	0.052	0.07	1.00					
S80T60	0.01	0.12	0.003	0.07	0.03	0.21	1.00				
S80T80	0.01	0.10	0.004	0.06	0.04	0.27	0.72	1.00			
S80T100	0.01	0.11	0.01	0.09	0.08	0.25	0.85	0.91	1.00		
S80T120	0.01	0.13	0.01	0.11	0.09	0.21	0.96	0.73	0.84	1.00	
S80T140	0.08	0.49	0.31	0.58	0.65	0.32	0.81	0.73	0.77	0.83	1.00
CAS40	0.003	0.02									
CAS60	0.002		0.0001								
CAS80	0.01			0.003		0.78	0.01	0.07	0.09	0.053	0.35
CAS100	0.01				0.11						
CAT40	0.01	0.01	0.005	0.01	0.01						
CAT60	0.004						0.04				
CAT80	0.004							0.04			
CAT100	0.002								0.07		
CAT120	0.005									0.24	
CAT140	0.001										0.12

Table S10. (continued)

P-value	CA S40	CA S60	CA S80	CA S100	CA T40	CA T60	CA T80	CA T100	CA T120	CA T140
CAS40	1.00									
CAS60	0.36	1.00								
CAS80	0.58	0.01	1.00							
CAS100	0.49	0.18	0.71	1.00						
CAT40	0.30	0.02	0.36	0.86	1.00					
CAT60	0.77	0.10	0.71	0.60	0.31	1.00				
CAT80	0.79	0.04	0.54	0.55	0.23	0.94	1.00			
CAT100	0.73	0.61	0.34	0.33	0.18	0.49	0.49	1.00		
CAT120	0.54	0.13	0.80	0.90	0.71	0.66	0.60	0.35	1.00	
CAT140	0.33	0.74	0.12	0.15	0.06	0.18	0.17	0.51	0.14	1.00

Table S11. Two tailed P-values for mean strain at break. Values in red indicate the difference in means between the two samples being compared is significant (α = 0.05).

P-value	CA	S40 T40	S60 T40	S80 T40	S100 T40	S80 Tn	S80 T60	S80 T80	S80 T100	S80 T120	S80 T140
CA	1.00										
S40T40	0.17	1.00									
S60T40	0.17	0.98	1.00								
S80T40	0.11	0.37	0.38	1.00							
S100T40	0.02	0.21	0.20	0.03	1.00						
S80Tn	0.81	0.17	0.18	0.13	0.02	1.00					
S80T60	0.72	0.18	0.18	0.12	0.02	0.95	1.00				
S80T80	0.11	0.75	0.73	0.23	0.36	0.12	0.12	1.00			
S80T100	0.11	0.54	0.56	0.58	0.0504	0.12	0.13	0.35	1.00		
S80T120	0.27	0.20	0.21	0.21	0.03	0.39	0.20	0.14	0.17	1.00	
S80T140	0.13	0.64	0.62	0.24	0.53	0.14	0.14	0.86	0.33	0.16	1.00
CAS40	0.95	0.17									
CAS60	0.22		0.22								
CAS80	0.15			0.38		0.21	0.16	0.16	0.24	0.42	0.18
CAS100	0.90				0.02						
CAT40	0.86	0.28	0.29	0.65	0.02						
CAT60	0.24						0.28				
CAT80	0.07							0.16			
CAT100	0.39								0.38		
CAT120	0.76									0.44	
CAT140	0.16										0.17

Table S11. (continued)

P-value	CA S40	CA S60	CA S80	CA S100	CA T40	CA T60	CA T80	CA T100	CA T120	CA T140
CAS40	1.00									
CAS60	0.20	1.00								
CAS80	0.14	0.60	1.00							
CAS100	0.81	0.08	0.09	1.00						
CAT40	0.77	0.07	0.08	0.93	1.00					
CAT60	0.25	0.40	0.50	0.23	0.23	1.00				
CAT80	0.06	0.33	0.89	0.004	0.01	0.52	1.00			
CAT100	0.40	0.67	0.83	0.36	0.35	0.68	0.87	1.00		
CAT120	0.79	0.35	0.23	0.61	0.58	0.28	0.12	0.45	1.00	
CAT140	0.15	0.65	0.93	0.08	0.08	0.48	0.79	0.80	0.24	1.00

Table S12. Mechanical properties of uncoated CA films treated under different conditions.

Sample	T_{spray} (°C)	$T_{thermal}$ (°C)	$F_B{}^a$ (N)	E^a (GPa)	$\sigma_y{}^a$ (MPa)	$\varepsilon_B{}^a$ (%)
CA	-	-	38.5 ± 0.8	2.39 ± 0.25	42.9 ± 5.9	3.3 ± 1.0
CAS40	40	-	41.5 ± 0.2	2.81 ± 0.03	57.6 ± 3.5	3.3 ± 0.8
CAS60	60	-	40.8 ± 0.1	2.78 ± 0.12	59.6 ± 1.3	4.0 ± 0.6
CAS80	80	-	40.7 ± 0.1	2.68 ± 0.11	56.5 ± 1.0	4.4 ± 0.9
CAS100	100	-	41.9 ± 0.5	2.61 ± 0.04	55.6 ± 3.4	3.2 ± 0.4
CAT40	-	40	40.4 ± 0.9	2.70 ± 0.07	55.2 ± 2.3	3.2 ± 0.4
CAT60	-	60	39.7 ± 4.4	2.77 ± 0.06	56.9 ± 2.2	5.6 ± 3.1
CAT80	-	80	41.8 ± 1.3	2.74 ± 0.04	57.0 ± 1.4	4.4 ± 0.4
CAT100	-	100	41.7 ± 0.6	2.76 ± 0.13	58.5 ± 3.6	4.7 ± 2.7
CAT120	-	120	41.1 ± 1.2	2.61 ± 0.04	56.0 ± 3.5	3.5 ± 0.9
CAT140	-	140	40.8 ± 0.9	2.72 ± 0.10	60.2 ± 3.6	4.3 ± 0.9

[a] The breaking force (F_B) was measured by a puncture testing (ASTM F1306). The modulus (E), yield stress (σ_y), strain at break (ε_B) values were obtained by a microtensile testing (ASTM D1708).

Supplementary analysis on mechanical properties

To separate the influences of the ChNW-CNC coating and the CA substrate on the mechanical properties, CA films were either sprayed with water or thermally treated at different temperatures and then characterized. It is shown in **Table S10** that the mechanical properties of treated CA were improved in comparison to untreated CA. The values of modulus, yield stress, and breaking force for CAS40 to CAS100 samples were on average 14%, 37%, and 7% higher than those of untreated CA, respectively, while the strain at break values were not significantly changed. Similar results were found for CAT40 to CAT140 samples. This is hypothesized to be the result of physical aging.

Furthermore, by comparing coated films with treated CA films, the values of modulus and the strain at break for relevant samples, e.g., S40T60 versus CAS40 and CAT60, were generally not significantly different. This also suggests the dominant role of the CA substrate on the mechanical properties. Overall, the yield stress values for coated films were lower than those of treated CA films, but the breaking force values showed the opposite trend, which verifies that the ChNW-CNC coating resulted in an improvement in the mechanical properties.

Table S13. Mechanical properties of common plastics for food packaging applications versus the coated film S80T140.

Sample	*E* (GPa)	σ_y (MPa)	ε_B (%)
PE, low-density, film grade[7]	0.14 - 0.48	8 - 22	50 - 1000
PE, high-density, film grade[7]	0.02 - 1.35	2.69 - 200	350 - 1700
PS, extrusion grade[7]	1.65 - 3.4	5.2 - 52.4	1 - 70
PP, film grade[7]	0.7 - 7.51	3.38 - 42.1	8 - 900
PVC, flexible grade[7]	0.006-3.23	0.12-50	16-700
PLA[7]	0.05-13.8	8-103	0.5-700
PET, unreinforced[7]	1.57 - 5.2	5.52 - 90	4 - 600
EVOH[7]	1.08 - 3.1	43 - 94	130-330
CA	2.39 ± 0.25	42.9 ± 5.9	3.3 ± 1.0
S80T140	2.73 ± 0.22	60.2 ± 3.6	11.3 ± 7.9

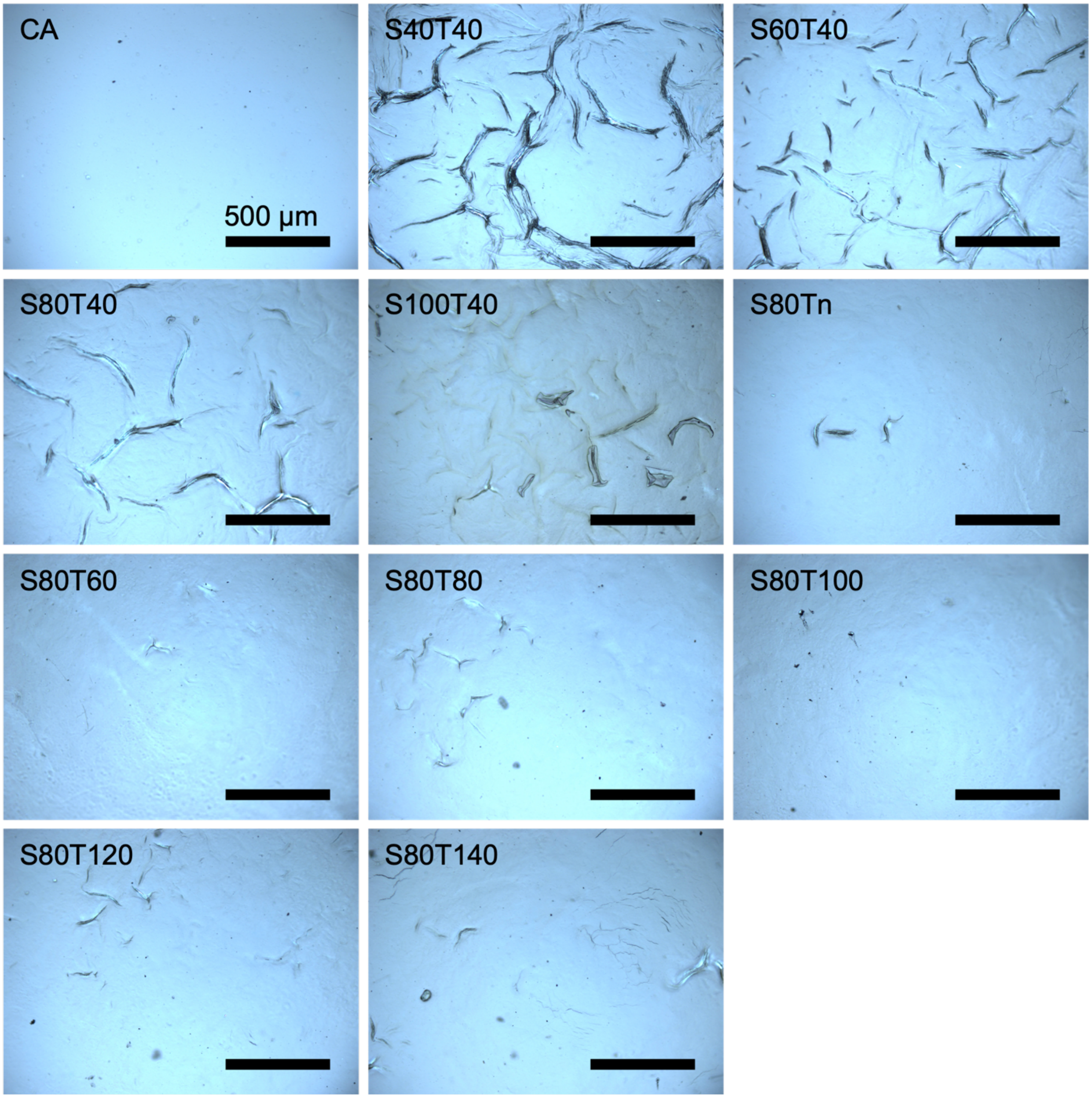

Figure S6. Optical microscope images for untreated CA and coated CA films. Scale bars: 500 µm.

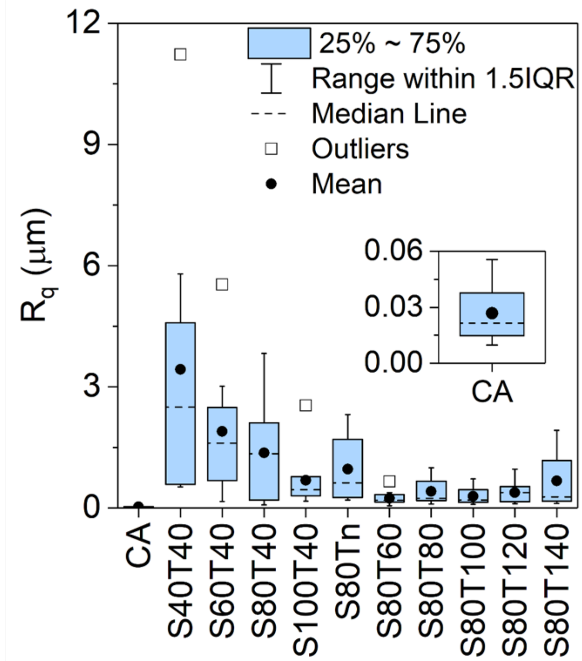

Figure S7. Root-mean-square roughness of surfaces of the untreated CA and coated CA films determined by profilometry. The inset zooms in on the roughness distribution of the untreated CA. The interquartile range (IQR) is the distance between the upper (75%) and lower (25%) quartiles of the dataset.

Table S14. Optical properties of common plastics for food packaging applications versus the coated film S80T140.

Film	Transmittance (%)	Haze (%)
PE, low-density, film grade[7]	55-90	1.1-55
PE, high-density, film grade[7]	-	4.0-81
PS, molded, unreinforced[7]	1-92	0.35-88
PP, film grade[7]	0.2-90	0.1-90
PVC, flexible grade[7]	80-90	2.5-14.3
PLA[7]	90	2.0-85
PET, unreinforced[7]	67-99	0.3-40
CA	92	1
S80T140	84	3

References

1. Technical information for cellulose acetate, Daicel Corp. https://www.daicel.com/cell_ac/en/detail/index.html (accessed 2022-07-04).
2. Ji, Y.; Waters, S.; Lim, E.; Lang, A. W.; Ciesielski, P. N.; Shofner, M. L.; Reynolds, J. R.; Meredith, J. C., Minimizing Oxygen Permeability in Chitin/Cellulose Nanomaterial Coatings by Tuning Chitin Deacetylation. *ACS Sustain. Chem. Eng.* **2022,** *10* (1), 124-133. DOI: 10.1021/acssuschemeng.1c05051

3. Liao, J. S.; Pham, K. A.; Breedveld, V., Rheological characterization and modeling of cellulose nanocrystal and TEMPO-oxidized cellulose nanofibril suspensions. *Cellulose* **2020,** *27* (7), 3741-3757. DOI:
4. Lange, J.; Wyser, Y., Recent innovations in barrier technologies for plastic packaging - a review. *Packag. Technol. Sci.* **2003,** *16* (4), 149-158. DOI: 10.1002/pts.621
5. Satam, C. C.; Irvin, C. W.; Lang, A. W.; Jallorina, J. C. R.; Shofner, M. L.; Reynolds, J. R.; Meredith, J. C., Spray-Coated Multilayer Cellulose Nanocrystal-Chitin Nanofiber Films for Barrier Applications. *ACS Sustain. Chem. Eng.* **2018,** *6* (8), 10637-10644. DOI: 10.1021/acssuschemeng.8b01536
6. Muller, J.; Gonzalez-Martinez, C.; Chiralt, A., Poly(lactic) acid (PLA) and starch bilayer films, containing cinnamaldehyde, obtained by compression moulding. *Eur. Polym. J.* **2017,** *95*, 56-70. DOI: 10.1016/j.eurpolymj.2017.07.019
7. MatWeb: Online Materials Information Resource, http://www.matweb.com (accessed 2022-05-05).