Electronic Supplementary Material (ESI) for RSC Sustainability

Low-water-permeability foils based on bio-renewable cellulose-derivatives

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1. Materials

Sodium carboxymethyl cellulose (CMC) with a degree of substitution of 1.2 and weight-average molecular weight of ~250,000 g/mol was obtained from Sigma Aldrich. ACS reagent grade citric acid (CA) monohydrate (≥ 99.0% pure) was obtained from Sigma Aldrich.

2. Methods

2.1 Film preparation

A parent CMC solution was prepared by dissolving 10.0 g CMC in 990.0 mL deionized water to yield a 1.0 wt% CMC solution. To prepare CMC films with different CA content, the appropriate amount of CA was dissolved in the CMC solution. CMC/CA mixtures were dried via drop casting in either polystyrene or Teflon (PTFE) dishes at ambient conditions. Samples containing 25 to 35 wt% CA adhered strongly to polystyrene drying dishes and could not be removed without damaging the samples. Conversely, samples with less than 25 wt% CA did not wet the PTFE dish during drying, resulting in deformed films that were very thick. Thus, we opted to use different drying substrates depending on the CA content – samples with 0 to 20 wt% CA were dried on polystyrene, while 25 to 35 wt% CA were dried on PTFE to enable production of films of comparable thickness. Dry films were peeled from the drying dish and prepared for characterization.

Heat-treated CMC/CA films were prepared by heating CMC/CA films in a convection oven at 120 °C for 2 hours to remove water and promote chemical reaction between CMC and CA.[1-4]

2.2 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was measured using a Nicolet 6700 FTIR equipped with a diamond crystal attenuated total reflectance (ATR) attachment. The absorbance was measured from 400 to 4000 cm^{-1} using 64 scans and a resolution of 4 cm^{-1}, and the resulting spectra were normalized by their maximum absorbance.

FTIR was measured for heat-treated CMC/CA films that were washed by soaking in an excess of deionized water to remove unreacted CA, and for heat-treated films that were treated with NaOH by soaking in NaOH solution with a pH of approximately 10. Additional NaOH was added as

necessary to maintain the pH at approximately 10 until the films were completely deprotonated. The films were considered fully deprotonated when the pH of the NaOH solution was constant at approximately 10 after soaking overnight.

The least acidic proton in CMC/CA films is the third carboxylic acid group on CA (pKa_3 = 6.4). At pH = 10, all carboxylic acid groups on both CMC and CA are expected to be completely deprotonated since the pH is well above the pKa of the least acidic proton.[5-7] Significant degradation of CMC is not expected at this pH.[8-10] It was not possible to treat neat CMC films with NaOH since they are fully soluble in water. Thus, a solution with pH of approximately 7 was used to prepare the neat CMC film for FTIR.

2.3 Water vapor transmission rate

CMC/CA films were prepared by adding the appropriate amount of CA to 25.0 mL of 1.0 wt% CMC solution to yield films with 0, 10, 25, 30, 35, and 40% CA by mass. Film edges were cut away with scissors, and film thickness was measured using a micrometer and reported as the average of at least 10 measurements at different points on the film. Each film was masked using adhesive aluminum foil allowing for 1.0 – 5.0 cm^2 of exposed film area depending on the sample and test condition. If needed, the films were softened to facilitate cutting and masking by exposing to water vapor using an Electrotech ultrasonic humidification system. The masked films were heat-treated as described previously and stored in a desiccator equipped with saturated magnesium nitrate to maintain 53% RH for at least one day before testing.

Water vapor transmission rate (WVTR) was measured at 23 °C using a MOCON PERMATRAN-W 1/50 WVTR Analyzer. The dry side humidity was maintained at 5% RH while the wet side humidity was set to 50, 65, 70, 75, or 80% RH. The WVTR was normalized for the thickness of the films according to **Equation 1**, where $WVTR$ is the thickness-normalized WVTR (g-mm/m^2-day), $WVTR_0$ is the absolute WVTR (g/m^2-day), and t is the average film thickness (mm).

$$WVTR = WVTR_0 \times t \qquad \textbf{Equation 1}$$

2.4 Soluble fraction

To measure their soluble fraction, heat-treated CMC/CA films were stored under vacuum (< –0.09 MPa) at ambient temperature in a desiccator equipped with indicating drierite desiccant for at least 72 hours and the mass of the dry films was measured. The films were soaked in an excess of DI water (approximately 100 mL) for at least 72 hours. An initial mass of 0.05 – 0.2 g was used for all CMC/CA films. The films were removed from the water bath, dried under ambient conditions, and stored in a vacuum desiccator for at least 72 hours. The mass of each film was measured again, and the dissolved fraction was calculated according to **Equation 2**, where m_1 is the mass of the dry film before s

$$Soluble\ fraction = \frac{m_1 - m_2}{m_1} \times 100 \qquad \textbf{Equation 2}$$

2.5 Residual water content

Residual water content was determined by calculating the mass loss of CMC/CA films when heated from 25 to 150 °C. Mass loss was measured using a Mettler Toledo TGA/DSC 3+ STAR system at a heating rate of 20 °C/min. Percent residual water content (RWC) was calculated

according to **Equation 3**, where m_{25} and m_{150} are the sample mass at 25 °C and 150 °C, respectively.

$$RWC = \frac{m_{25} - m_{150}}{m_{25}} \times 100$$

Equation 3

2.6 Mechanical properties

Mechanical properties (upper tensile strength, strain at break, and Young's modulus) were measured using a high-throughput mechanical characterization (HTMECH) instrument, described previously.[11] In short, CMC/CA and CMC/CA/HT films were sandwiched between two perforated plates. The samples were punctured by a blunt needle through the perforated plates at different locations on the film. The force, displacement, and contact time were used to calculate stress/strain behavior of the films. Measurements were repeated at least 8 times per sample.

3. Supplementary data

Table S1: Water vapor transmission rates (WVTR) of films at different experimental conditions and with different curing temperatures (T_c).

Material	T_c °C	RH %	T °C	WVTR g-mm/m^2-day	Reference
CMC	120	50	23	25.5	This work
CMC/CA10	120	50	23	1.5	This work
CMC/CA25	120	65	23	0.02	This work
CMC	60	50	14	47.9	[12]
	40	50	25	192	[13]
	N/A	97	25	381	[14]
Cellulose nanofibril	N/A	50	--	9.8	[15]
	N/A	50	23	22	[16]
	175	100	40	203	[17]
	N/A	50	23	7	[18]
	145	50	23	0.16	[19]
	170	50	23	1.7	[18]
Cellulose nanofibril/chitosan/CA	N/A	50	23	24.3	[20]
Cellulose acetate	N/A	50	20	~10.4	[21]
	N/A	90	20	22.12	[21]
Cellulose butyrate	N/A	50	20	~1.1	[21]
	N/A	90	20	17.97	[21]
Cellulose propionate	N/A	50	20	~6.9	[21]
	N/A	90	20	21.54	[21]
Poly(ethylene terephthalate)	N/A	50	23	0.16	This work
	N/A	85	23	0.5 – 2	[22]
	N/A	--	--	1.2	[23]
	N/A	90	38	0.4 - 8	[24]
	N/A	--	--	0.79	[23]
High density polyethylene	N/A	--	25	0.0148	[25, 26]
	N/A	90	38	0.14 – 0.30	[23]
Low density polyethylene	N/A	--	25	0.112	[25, 26]
	N/A	100	38	0.589 – 0.766	[23]
Polypropylene	N/A	85	23	0.2 – 0.4	[22]
	N/A	90	38	0.7 – 2	[24]
Poly(vinyl chloride)	N/A	--	25	0.451	[25]
	N/A	90	38	< 1.6	[23]
	N/A	85	23	1 – 2	[22]
Poly(vinylidene chloride)	N/A	--	--	0.025 – 0.913	[25]
	N/A	--	--	0.065	[23]
	N/A	85	23	0.1	[22]
	N/A	90	38	1.7	[24]
	N/A	100	27	0.04	[15, 27]
	N/A	--	--	0.11	[23]

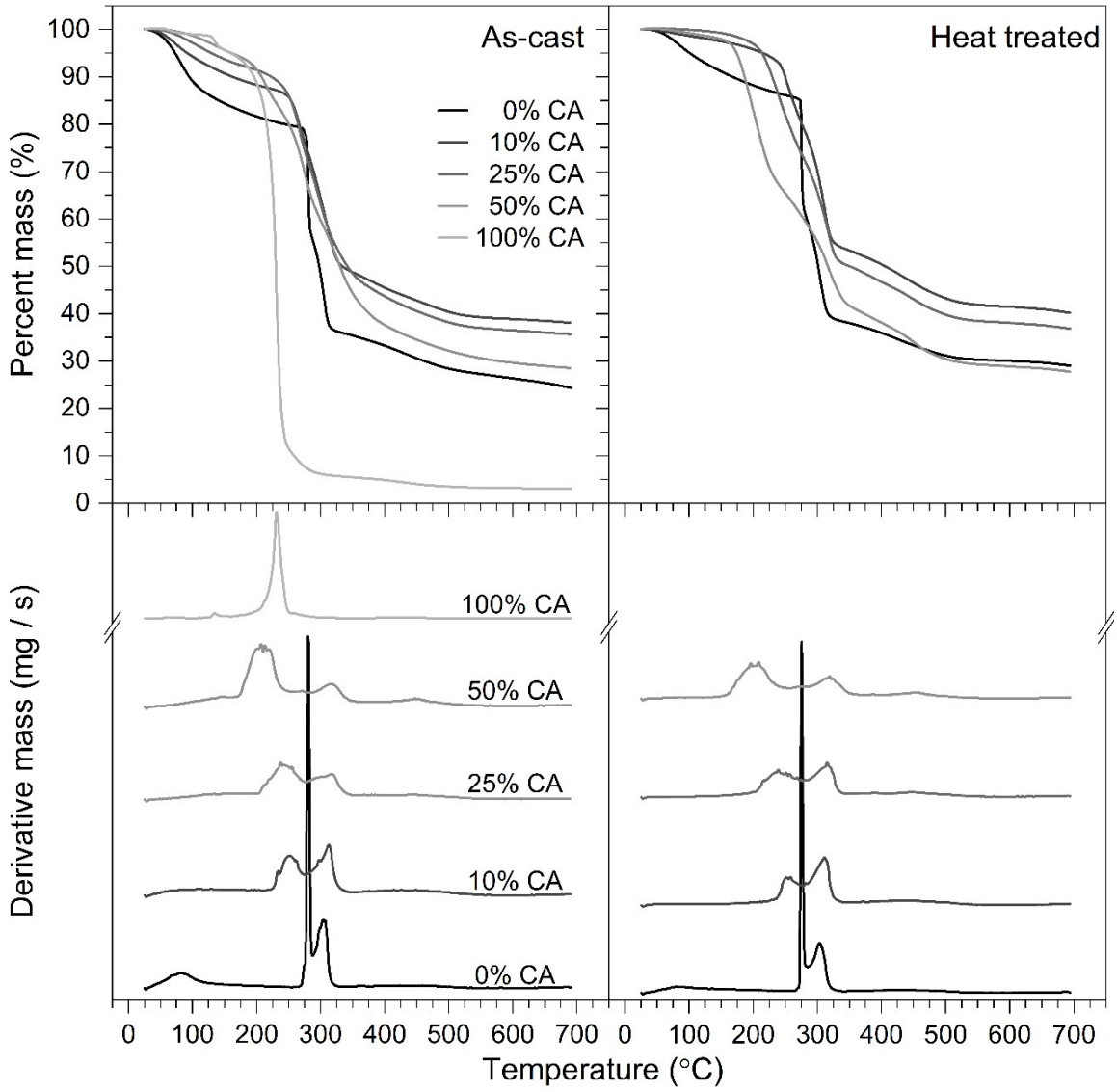

Figure S1: Thermogravimetric analysis (top) and derivative mass (bottom) of CMC films with different amounts of CA before (left) and after (right) heat treatment measured using TGA. CA monohydrate represents the neat CA sample for reference.

Table S2: Tensile strength (TS), strain at break (SAB), and Young's modulus (YM) of CMC/CA films before and after heat-treatment. Values represent the average and standard deviation (σ) of at least eight measurements.

CA content (wt%)	Sample set	TS (MPa)	σ_{TS}	SAB (%)	σ_{SAB}	YM (GPa)	σ_{YM}
0	As-cast	39.7	3.2	27.7	4.6	0.6	0.1
0	Heat-treated	38.6	3.0	56.7	13.3	0.2	0.2
0	75% RH	38.0	2.1	18.2	2.6	0.7	0.2
10	As-cast	49.8	2.4	7.5	1.7	1.9	0.4
10	Heat-treated	36.8	11.2	2.8	1.0	2.7	0.7
10	75% RH	33.0	3.4	7.9	1.3	0.7	0.3
25	As-cast	25.6	15.4	4.6	4.1	8.1	5.7
25	Heat-treated	11.3	1.3	1.3	0.7	2.8	1.7
25	75% RH	10.3	1.9	5.1	0.9	0.7	0.4
50	As-cast	25.0	3.0	11.7	4.9	0.7	0.3
50	Heat-treated	11.6	3.4	1.6	0.8	3.4	1.5
50	75% RH	4.6	0.5	13.2	1.2	0.1	0.02

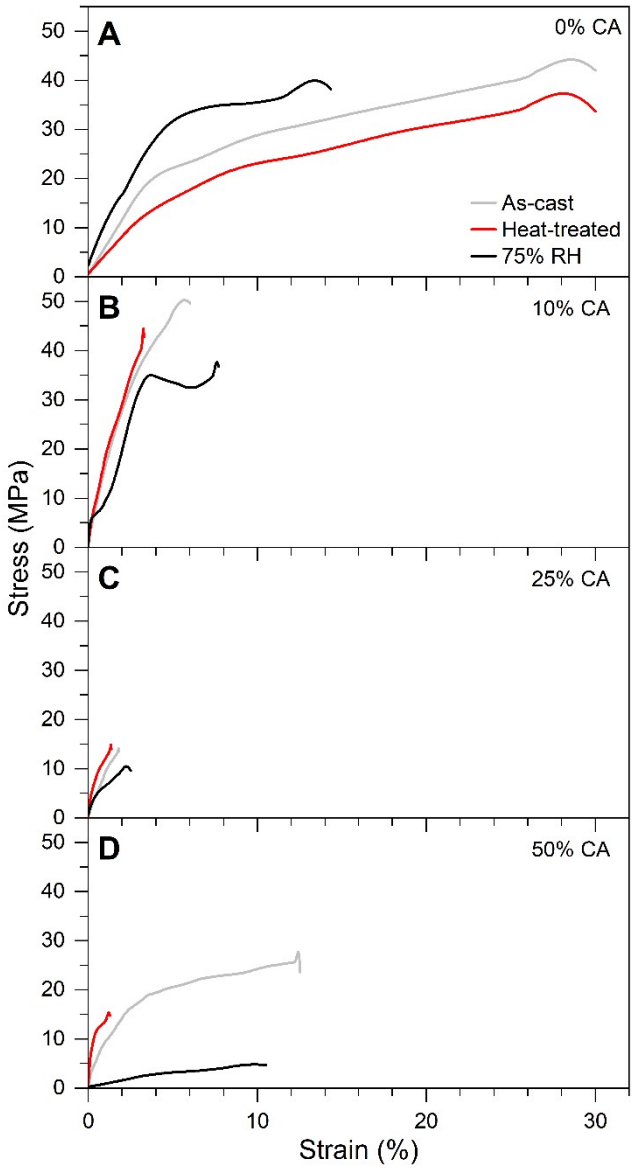

Figure S2: Tensile properties of CMC/CA films containing **A)** 0wt% CA, **B)** 10 wt% CA, **C)** 25 wt% CA, and **D)** 50 wt% CA before (grey lines) and after (red lines) heat treatment, and at 75% RH (black lines).

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