Electronic Supplementary Information (ESI)

Bioinspired self-assembled films of carboxymethyl cellulose-dopamine/montmorillonite

Tianyu Guo[a], Lihui Gu [a], Yu Zhang [a], Hui Chen [a], Bo Jiang [a], Huifang Zhao [a], Yongcan Jin*[a] and Huining Xiao*[b]

[a] Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Nanjing Forestry University, Nanjing 210037, China

[b] Department of Chemical Engineering, University of New Brunswick, Fredericton, E3B 5A3, NB Canada

* jinyongcan@njfu.edu.cn, hxiao@unb.ca

The residual carboxyl content of CMC grafted with DA was determined using a conductimetric titration method. [1, 2, 3] In brief, a desired amount of 0.1 M HCl solution was added to 50 mL of 0.1 wt% DA-CMC solution to adjust the pH in the range of 2.5-3.0, which could fully acidify the salt-based samples. Then, 0.05 M NaOH was added at the rate of 0.1 mL/min until the pH reached 11 using a titration apparatus. Typical titration curves are shown in Figure S1. These curves allow us to calculate the carboxylate content (A, mmol/g), which is given by Eq. (1),

$$A = \frac{(V_2 - V_1) \times C_1}{m \times C_2} \times 10^{-6} \tag{1}$$

where V_1 and V_2 are the amount of NaOH (mL, see Figure S1); C_1 is the NaOH concentration (mol/L); m (g) is the weight of the sample solution; C_2 is the mass fraction of DA-CMC.

The method of determining the water solubility (WS) was based on that reported by Gontard et al. previously.[4] In brief, samples were cut into square shapes (2 cm^2) and dried at 105 °C for 24 h, before and after the solubilization period. After each drying period, samples mass was measured using an analytical balance. Three replicates were made to each film. The WS was calculated using Eq. (2):

$$WS = \frac{Q_0 - Q_1}{Q_0} \times 100\ \% \tag{2}$$

where Q_0 refers to the first dried material (before the solubilization) and Q_1 refers to the dried material after a desired time of solubilization.

To identify the influence of DA dosage on the degree of grafting on CMC, different amounts of DA (1.0, 3.0, and 5.0 mmol) were added. The resulting DA-CMC samples were coded as DA-CMC1, DA-CMC2, and DA-CMC3, respectively. Typical titration curves demonstrated the presence of strong and weak acid groups. As shown in Table S1, the carboxyl content of CMC was 3.28 mmol/g, which was decreased with the increasing of conjugated amount of DA in DA-CMC. After conjugated with DA at different amounts, the residual carboxyl contents on CMC surfaces were 2.75, 1.96, and 1.89 mmol/g cellulose for DA-CMC1, DA-CMC2, and DA-CMC3, respectively. Since the initial content of CMC was already known, the portion of DA grafted on CMC for DA-CMC3 was found to be ca. 42% based on the reduction of carboxyl contents (presumably the DA substituted the carboxyl groups on CMC exclusively). Therefore, the degree of grafting is reasonable in the current systems. For the effect of DA dosage on the properties of films, the similar work previously published elsewhere[5, 6] indicated that increasing the amount of conjugated DA between "mortar" and "brick" structures led to high interfacial adhesion even at higher RH. Since this effect is well known, in the current system, we chose the DA-CMC with the highest DA content to explore the properties (e.g. hygromechanical and fire retardancy) of DAC/M films.

Tables and Figures

Table S1. Carboxyl content (mmol/g) of the CMC-DA conjugate solutions prepared with different initial amounts of DA.

Samples	Carboxyl content (mmol/g)	
	Before	After
CMC	3.28	-
DA-CMC1	3.28	2.75
DA-CMC2	3.28	1.96
DA-CMC3	3.28	1.89

Table S2. UV-Vis percent transmittance of DAC/M films at 400 nm and 600 nm.

Samples	Transmittance (%)	
	400 nm	600 nm
7DAC/3M	24.1	40.0
5DAC/5M	17.3	30.8
3DAC/7M	14.9	17.2
1DAC/9M	11.2	12.8

Table S3. Mean values ± standard deviation of soaking time (h), water solubility (%) and thickness (μm) of film

Sample	Soaking Time (min)	Water Solubility (%)	Thickness (μm)
5CMC/5M	20	18 ± 2	33 ± 0.1
	40	32 ± 2	33 ± 0.2
	60	43 ± 3	32 ± 0.1
	80	54 ± 4	33 ± 0.2
	100	dissolved	34 ± 0.2
	120	dissolved	33 ± 0.1
	140	dissolved	32 ± 0.1
	160	dissolved	33 ± 0.2
	180	dissolved	33 ± 0.2
5DAC/5M	20	5 ± 2	27 ± 0.1
	40	7 ± 2	28 ± 0.2
	60	12 ± 2	28 ± 0.1
	80	16 ± 2	27 ± 0.2
	100	18 ± 2	28 ± 0.1
	120	20 ± 3	28 ± 0.1
	140	24 ± 2	27 ± 0.2
	160	29 ± 3	28 ± 0.2
	180	31 ± 3	28 ± 0.1

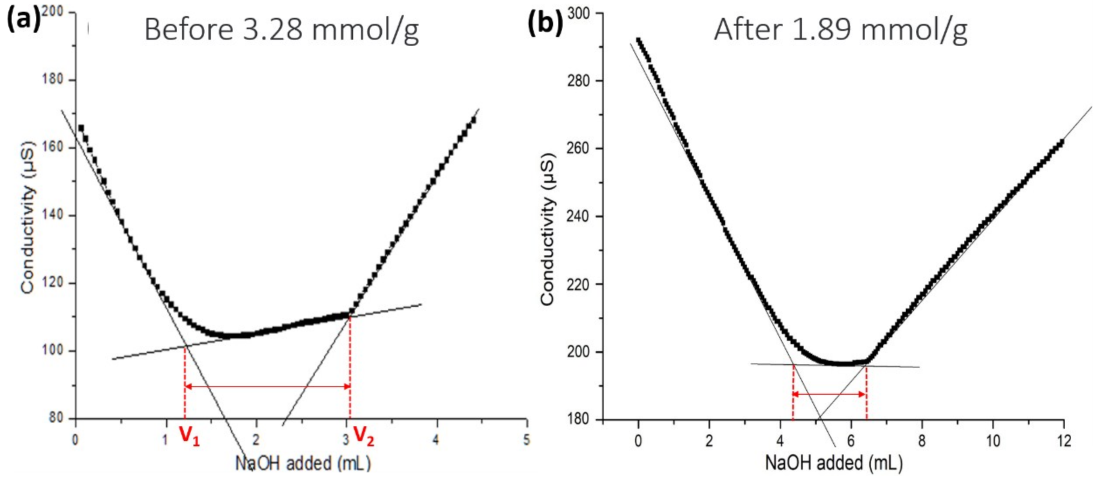

Figure S1. Conductometric titration curve for (a) CMC and (b) DA-CMC3

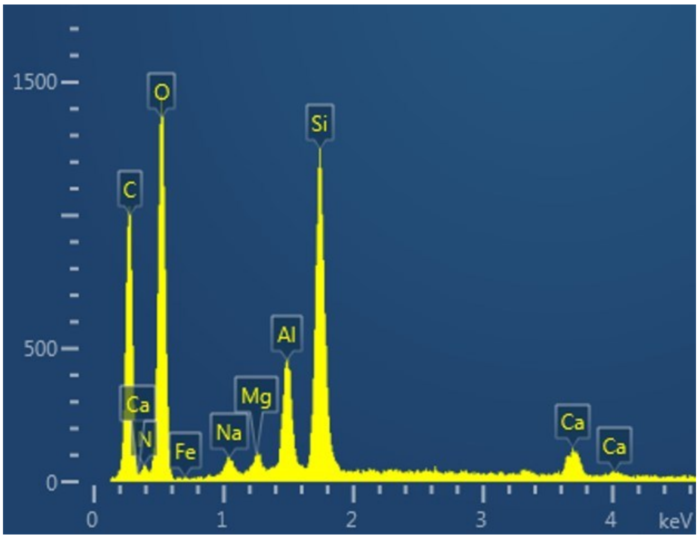

Figure S2. EDC spectra for 5DAC/5M

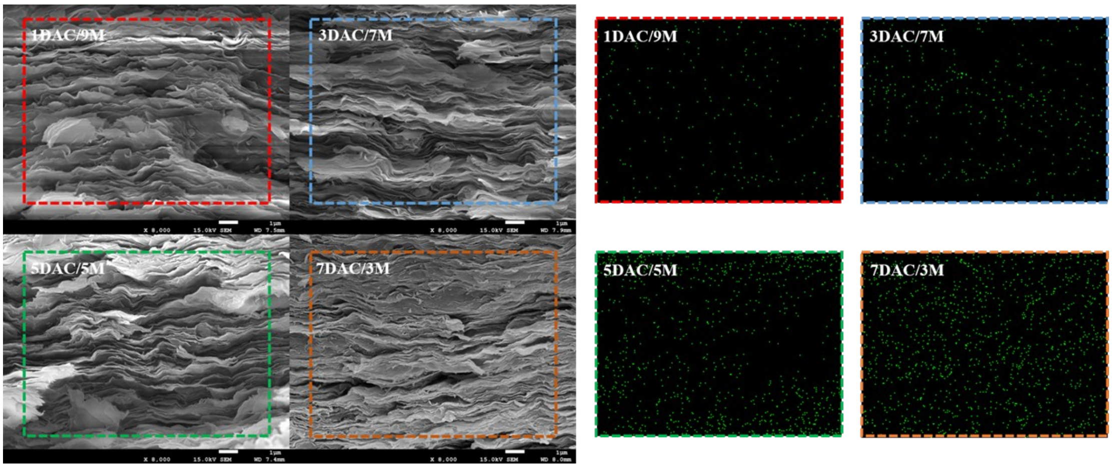

Figure S3. SEM-EDS mapping indicating uniform distribution of nitrogen in composite film.

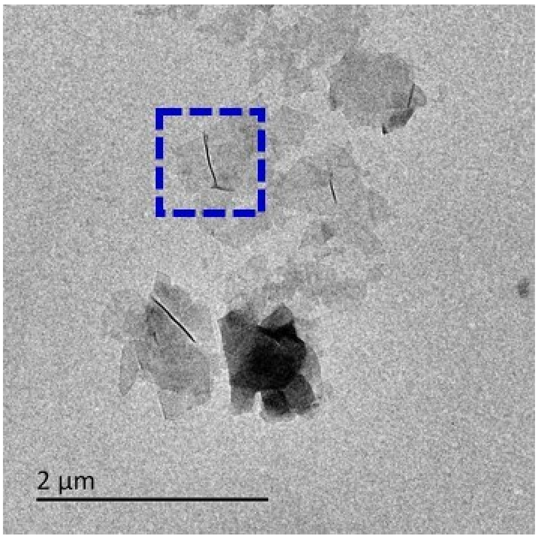

Figure S4. TEM image for 5DAC/5M

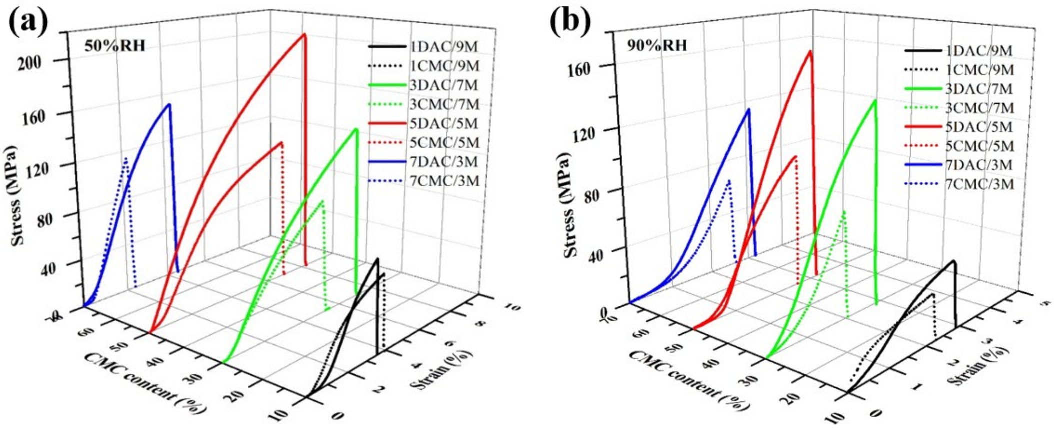

Figure S5. Representative stress-strain curves from tensile test at the relative humidity of (a) 50% and (b) 90%.

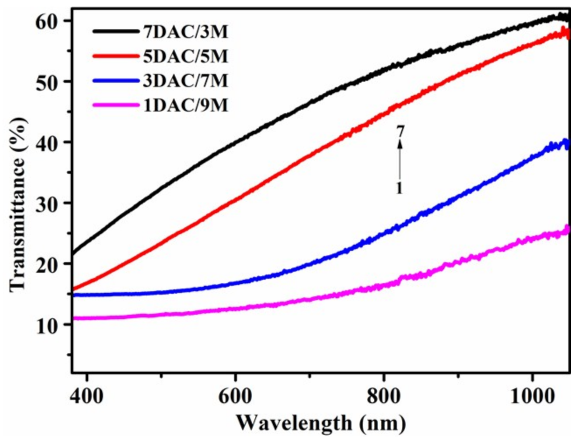

Figure S6. UV-Vis spectra of DAC/M films with different weight ratios

References

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