Electronic Supplementary Information

for

Phase-specific pore growth in ultrathin bicomponent films from cellulose-based polysaccharides

by

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ESI includes atomic force microscopy (AFM) images of the TMSC/CTA 1:0, 2:1 and 0:1 films prepared under varying relative humidity (Figure S1), AFM height images of the TMSC/CTA 10:1 blend film before and after annealing for 24 hours (Figure S2), X-ray photoelectron spectroscopy (XPS) spectra for the Cellulose/- films (Figure S3), surface roughness data (Figure S4 and Table S1) and comparison of measured and calculated water contact angles (Table S2).

S1 - The effect of total polymer concentration. In order to investigate whether the total polymer concentration played a role in the morphology formation under humid air, TMSC/CTA 1:0, 2:1 and 0:1 films with the same total polymer concentration in the initial spin coating solution (0.75 %) were produced (Figure S1). The film morphologies are similar to the ones with varying total polymer concentrations (TMSC/CTA 1:0 and 0:1 with 0.5 %, Figure 1) thus the effect of the total polymer concentrations could be eliminated from the results.

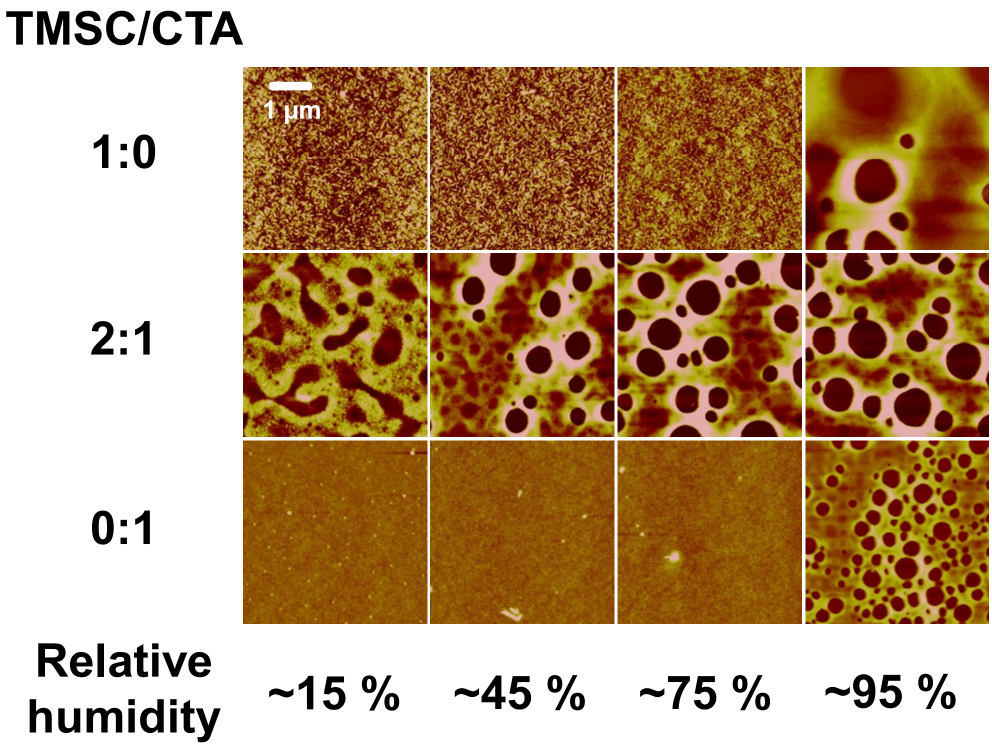

Figure S1. The effect of the humidity on the TMSC/CTA films (blend ratios 1:0, 2:1 and 0:1). All the films are prepared from the same total polymer concentration, 0.75%.

S2 - Annealing. The occurrence of dewetting as the original reason behind the phase separation in the films of can be effortlessly confirmed by annealing the films over the glass transition temperature (T_g) of CTA (minority, island-forming component). The T_g of the CTA used was determined with differential scanning calorimetry (DSC). The cellulose/CTA 10:1 film was annealed in 200 °C for 24 hours under constant nitrogen flow. No additional dewetting was noticed; only slight softening of the CTA domains (Figure S2).

Electronic Supplementary Material (ESI) for Soft Matter

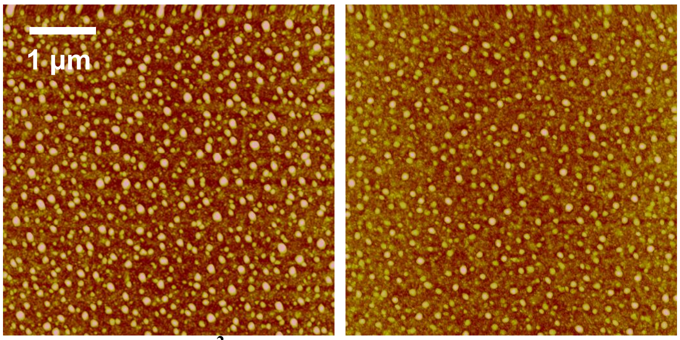

Figure S2. 5 × 5 µm^2 AFM height images of the Cellulose/CTA 10:1 film before (left) and after (right) annealing at 200 °C under nitrogen flow.

S3 - XPS spectra. From the XPS background signal, information on the coverage of the solid support by the film can be extracted.[S1] All other films were covering the solid support except the Cellulose/- films blend ratios 1:2, 1:5 and 1:10. In other words, when there were holes in the film, the background signal had increased noise level (Figure S3). The increase in noise is due to differences in charging behavior of the bare oxidized silicon substrate and cellulose surfaces.

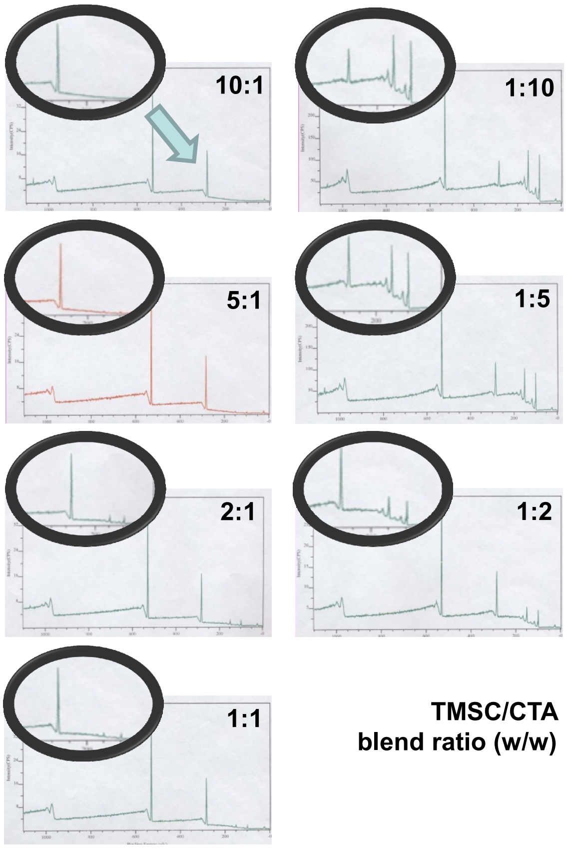

Figure S3. XPS spectra of the Cellulose/- films. The Cellulose/- films blend ratios 1:2, 1:5 and 1:10 have increased noise level in the background.

S4 - Surface roughness is an important parameter affecting the contact angles of liquids on solid substrates. The roughness effect is quantitatively expressed in the form of Wenzel equation:[S2]

$$\cos\theta^* = r\cos\theta \qquad \text{(S1)}$$

Where θ^* is the apparent contact angle (with the roughness influence), r is the roughness parameter defined as the ratio of true surface area vs. projected surface area, and θ is the contact angle for the ideal (smooth) surface.

The Figure S4 reveals that the roughness of the bicomponent films varies substantially depending on the blend ratio; the rms roughness fluctuates between 0.3 nm and 31.9 nm. Corresponding, calculated r values from the Wenzel equation (S1) are presented in Table S1. The true surface areas were determined with the help of Nanoscope Analysis software. Contact angles for the ideally smooth surface were then calculated from the Wenzel equation (S1). The difference in contact angle due to roughness effect is small, on the same scale with standard deviation from the measurements.

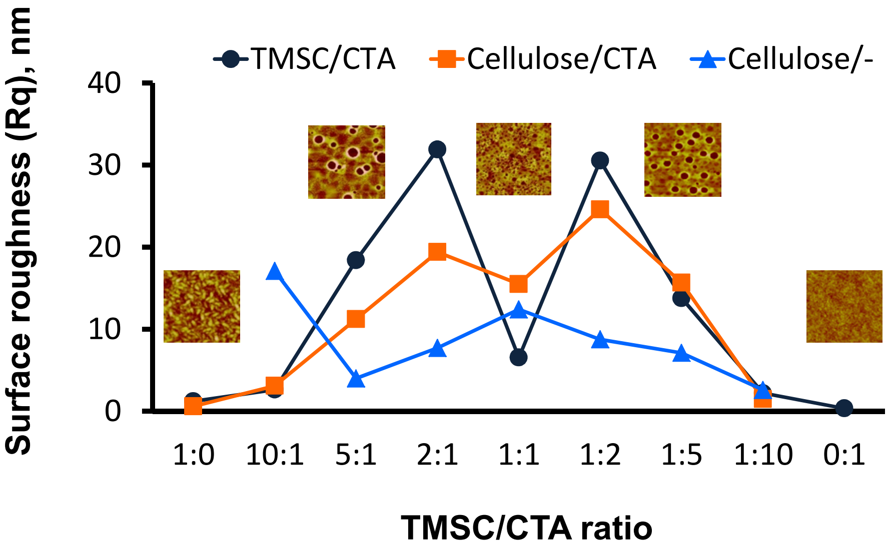

Figure S4. The surface roughness of the TMSC/CTA films (dark blue ●), Cellulose/CTA film (orange ■) and Cellulose/- films (light blue▲). The lines are added to guite the eye.

Table S1. Wenzel r parameters for the bicomponent TMSC/CTA films.

TMSC/CTA blend ratios	TMSC/CTA films	Cellulose/CTA films	Cellulose/- films
1:0	1.004	1.000	
10:1	1.010	1.005	1.037
5:1	1.015	1.015	1.006
2:1	1.095	1.036	1.007
1:1	1.006	1.018	1.006
1:2	1.099	1.042	1.008
1:5	1.021	1.027	1.013
1:10	1.000	1.000	1.010
0:1	1.000		

Table S2. Experimentally determined apparent water contact angles (AWCA) and contact angles calculated from Wenzel equation (WCA).

	TMSC/CTA films		Cellulose/CTA films		Cellulose/- films	
TMSC/CTA blend ratio	**AWCA, degrees**	**WCA, degrees**	**AWCA, degrees**	**WCA, degrees**	**AWCA, degrees**	**WCA, degrees**
1:0	93.3	93.3	58.6	58.6		
10:1	93.3	93.3	63.2	63.3	55.1	56.5
5:1	91.5	91.5	55.9	56.4	57.8	58.0
2:1	92.1	91.9	51.8	53.3	57.6	57.8
1:1	92.4	92.4	47.0	47.9	54.8	55.1
1:2	92.2	92.0	61.1	62.3	55.2	55.6
1:5	92.1	92.1	62.2	63.0	57.5	58.0
1:10	91.5	91.5	50.0	50.0	58.4	58.7
0:1	57.5	57.5				

References

(S1) Tougaard, S. *Surf. Interface Anal.*, 1998, **26**, 249-269.

(S2) Wenzel, R. N. *Ind. Eng. Chem.*, 1936, **28**, 988-994.