The preparation of ultrathin (<100 nm) bicomponent films from hydrophobic polysaccharides with phase-specific pore growth was demonstrated and the underlying phenomena behind morphology formation were fundamentally investigated. The films were constructed, in a single-step process, by spin coating mixtures of trimethylsilyl cellulose (TMSC) and cellulose triacetate (CTA) from a common solvent. Atomic force microscopy (AFM) revealed a nano- and micron-scale phase separated structure, typical for interfacial polymer blends. Vertical phase separation had resulted in a continuous layer of TMSC next to the substrate with laterally phase separated CTA and TMSC on top. Furthermore, X-ray photoelectron spectroscopy (XPS) and contact angle measurements indicated the presence of a thin overlayer of TMSC. In addition, increased relative humidity conditions during spin coating resulted in the formation of pores when the CTA weight percent in the blend was in the range from 17 to 83% (*i.e.*, in TMSC/CTA blend ratios 5 : 1, 2 : 1, 1 : 2, and 1 : 5). Closer analysis of the morphology indicated that the pores resided exclusively in the CTA phase. Hypothetically, the formation of the observed peculiar morphologies was ascribed to various phenomena occurring upon spin coating: vertical and lateral polymer phase separation, dewetting under humid atmosphere, and layer inversion during dewetting. It is concluded that the obtained ultrathin polysaccharide films with tailored surface pores, morphology and wettability are expected to be useful in emerging nanotechnologies while having the advantage of an effortless manufacturing process.

**Introduction**

Construction of polymeric bicomponent surfaces is a challenging field in materials science and technology. Their usage varies from organic light emitting diodes\(^1\) and photovoltaics\(^2\) to templates for controlled drug release.\(^3\) The ways to prepare bicomponent surfaces are diverse, including lithographic techniques,\(^4\) surface instabilities,\(^5\) spin coating polymer blends\(^6\) or block copolymers,\(^7\) and Langmuir–Blodgett deposition.\(^8\)

Another feature, which has been extensively surveyed in films and 2D structures, is porosity. With varying length scales from angstrom to micrometre scale, porous films are used for applications such as membranes,\(^9,10\) antireflective coatings,\(^11\) and templates for nanoparticle growth,\(^12\) to name but a few. The range of manufacturing methods is vast, with examples including utilizing of breath figures,\(^13\) block copolymer films,\(^7,14\) and chemical vapor deposition.\(^14\) Combining various length scales provides the potential to create hierarchical structures for high-tech applications. In this contribution, we will demonstrate the construction of a bicomponent ultrathin (<100 nm) film with micron-scale lateral phases where pores can be introduced selectively to cellulose after the film deposition by simple hydrolysis steps with vapor phase reagents.

The preparation of these bicomponent porous films is based on spin coating of polymer blend solutions. It is a facile one-step method to simultaneously induce, construct and possibly even align domains rich in various blend components. The surface patterns in spin coated ultrathin films of binary polymer solutions emerge from the complex interplay between the two polymer components, the solvent and the substrate and they are facilitated by the thermodynamic instability driven by spin coating.\(^15–17\) Conventionally, porosity in polymer blend films is obtained by dissolving the other component with a selective
In this paper, pores are grown directly and spontaneously on one of the polymer components in the film. Two cellulose derivatives were employed in the development of the films, trimethylsilyl cellulose (TMSC) and cellulose triacetate (CTA) (Chart 1). Both TMSC and CTA can be selectively converted to cellulose and they can be dissolved in a common solvent, a prerequisite for forming a supported ultrathin film from a polymer blend. Cellulose (Chart 1) has recently attracted wide attention as a native source for nanomaterials with peculiar qualities, such as unusual strength properties and liquid crystalline characteristics. Equally interesting is the use of cellulose in ultrathin films. Conventionally, nanocellular objects are constructed by top-down breakdown of the native structures but spin coating blends of hydrophobic cellulose derivatives is an effortless bottom-up method to prepare micro- and nanoscopic cellulose 2D structures. Here, we aim at fundamental understanding of pattern formation in the ultrathin films containing CTA and TMSC on solid supports and we explore the humidity-induced pore growth which is specific to the phase enriched in CTA. Since the phases can be explicitly transformed to cellulose, it is possible to utilize the unique characteristics of cellulose, which broadens the scope of the potential applications for these films. Other systems which are potentially capable of phase-specific pore growth are homopolymer/block copolymer blends. However, one-step, humidity-controlled pore growth on a specific phase during spin coating omits the synthetic complexities of block copolymers. Moreover, as the literature of ultrathin blend films is dominated by synthetic polymers, the use of renewable and widely available polysaccharides promotes the sustainable aspect in nanotechnology.

**Results and discussion**

The effect of humidity during spin coating on polysaccharide bicomponent thin film morphology formation was studied with four different relative humidity (RH) values and three TMSC/CTA blend ratios as well as neat TMSC and CTA films (TMSC/CTA 1 : 0, 10 : 1, 2 : 1, 1 : 10 and 0 : 1). Representative atomic force microscopy (AFM) height images of the bicomponent TMSC/CTA films spin coated under ambient air of low (~15%) and high (~95%) RH are shown in Fig. 1. The effect of humidity on the film morphologies of this bicomponent system was evident, especially in the case of the TMSC/CTA blend ratio 2 : 1. Increasing humidity enhanced the pore growth. The influence of humidity was downplayed in the films prepared from the neat components (TMSC or CTA) and in the blend films produced with one dominant or excess component. Observed porous morphologies did not emerge due to differences in the total polymer concentration; they are linked essentially to the humidity and the blend ratio. This was confirmed by producing TMSC/CTA 1 : 0, 2 : 1 and 0 : 1 films with the same total polymer concentration in the initial spin coating solution (Fig. S1, ESI†).

Neat TMSC and CTA films were observed to be smooth and featureless when the ambient air during spin coating was of low or medium RH. At ~15% RH, the rms roughness for TMSC and CTA was 1.3 and 0.3 nm, respectively. However, when the two components were mixed at varying ratios and spin coated on hydrophilic silica substrate, diverse morphologies emerged due to changes in RH and immiscibility of the solid polymers with each other, leading to phase separation. All the blend ratios underwent pore formation when spin coating was carried out at the highest ambient air humidity. At ~95% RH, pores with diameter up to ca. 2 µm emerged. In the blend ratio TMSC/CTA 1 : 10, the pores appeared already at the ~75% RH, in contrast to the behavior of, e.g., the symmetrical blend ratio TMSC/CTA 10 : 1. Jaczewska and co-workers found that different water uptakes by various polymer rich phases play a significant role in the morphology formation during spin coating under high humidity. The CTA-rich phase seemed to be more affected by the humidity. Furthermore, when the amount of CTA in the films was above a given critical concentration, the pore formation was enhanced. Interestingly, as noted above, films of neat CTA or films with excess of CTA, namely TMSC/CTA 1 : 10, did not form pores at ~45% RH. The unique layer structure observed for the TMSC/CTA blend ratio 2 : 1 seemed to trigger the pore growth.

Medium humidity (~45% RH) was chosen for further examination of the morphologies produced by hydrophobic polysaccharides after spin coating. Not only is this humidity more common in ambient conditions but also the diversity of the topographies formed on the surface of the films made were more amenable for further investigation. Fig. 2 shows bicomponent films prepared from TMSC/CTA blends with mass ratios 10 : 1, 5 : 1, 2 : 1, 1 : 2, 1 : 5 and 1 : 10 directly after spin coating and after modification steps. Two sample groups could be identified based on the emerging morphologies: films with excess of one component (TMSC/CTA 10 : 1 and 1 : 10) and intermediate blend ratio films (TMSC/CTA 5 : 1 : 1 : 5). The former morphology was characterized by the nanoscale features: islands (TMSC/CTA 1 : 10) or valleys (TMSC/CTA 10 : 1) and the latter by the formation of micron-scale pores (TMSC/CTA 5 : 1 : 1 : 5). The chemistry of the films could be tuned by converting the cellulose derivatives back to cellulose. The hydrolysis of TMSC to cellulose is well understood and quantitative conversion can be easily accomplished without any washing steps. Selective hydrolysis of TMSC leading to a vertical contraction of the TMSC-rich phase (I modification step) and dissolution of CTA (II modification step) enabled more straightforward distinction of each component.

The TMSC-rich phase contracts significantly during conversion to cellulose when the bulky trimethylsilyl groups are replaced by compactly packed hydroxyl groups (Chart 1). However, the intermediate blend ratios (TMSC/CTA 5 : 1 : 1 : 5) exhibited only minor visible changes after the conversion of...
When films are heated above a glass transition temperature ($T_g$) of the minority component, and kept in the oven for 24 hours no additional dewetting should occur and this was also the case in this work (Fig. S2, ES1).

As for the intermediate blend ratios (TMSC/CTA 5 : 1 : 1 : 5), the transient bilayer theory alone could not explain the morphology. An additional pore growth step occurred in the presence of humid air, and alternative mechanisms for pore growth have been proposed. Typically, the pore formation under high RH conditions and slow evaporation rate is attributed to the breath figure formation. Breath figures are usually ordered imprints of condensed water droplets on top of the substrate being cooled down during the solvent evaporation. Characteristic times for film preparation by typical breath figure setup and spin coating used in this work are in the scale of minutes and seconds, respectively. Hecht et al. have attributed porous morphologies in ultrathin spin coated films fabricated under high RH to dewetting, i.e., rupture of a thin liquid film. (We stress here that this hypothetical dewetting leading to pore formation is spatially and chronologically different to the dewetting occurring during phase separation.) Overall, the effect of humidity on structures formed by spin coating has been reported to a limited extent.

Further information on the morphology was obtained by studying the film thickness extracted from AFM images (Fig. 3). The height profiles are representative, individual line scans from the height images where part of the film had been scratched to expose the solid silicon support. Furthermore, the thickness profiles provide information on the presence and distribution of the two components in the films. This was most evident in the case of the TMSC/CTA blend ratios 10 : 1 and 1 : 10, where the majority component defined the way the morphology altered during the modification steps. The interpretation of the behavior of the intermediate blend ratios (TMSC/CTA 5 : 1 : 1 : 5) is more ambiguous. The pores did not penetrate down to the substrate in most cases, only when the amount of TMSC in the spin coating solution was low enough. The height of the CTA rich rims surrounding the pores varies approximately from 20 nm in untreated films to 100 nm in Cellulose/CTA films. The rims disappeared after the selective CTA dissolution.

Two hypotheses on the origins of film morphology are strengthened by the height profiles in Fig. 3: (i) the pores were concentrated in the CTA-rich phase since they were removed by selective dissolution of CTA and (ii) the pore formation appears to have been driven by a dewetting mechanism rather than breath figure formation because the high rims around the pores are characteristic of dewetted structures. The rims emerged when the polymer material was removed from the center to the edge of the pores upon dewetting. Their occurrence suggests that the presence of humid air induced a set of pores to nucleate at a later stage of film formation, i.e., when most of the solvent had already evaporated. The polymer was no longer mobile enough for the film to level out.

The density of the pores increased with the increasing amount of CTA in the spin coating solution and in the films (Fig. 4). This
concurs with the observations based on Fig. 2 and 3 that the pores appear exclusively in the CTA-rich phase. A number of studies have applied additional annealing steps after spin coating in order to provoke dewetting and consequent pore growth within the film. Quantitative comparison of the pore densities from those works to the ones in this work is, however, difficult because the mechanisms are intrinsically different. In our study, pore growth was facilitated by increased RH and it took place during spin coating whereas in the study by Thickett et al., for example, top and bottom layers were spin coated separately and the bilayer structure was annealed to initiate nucleation leading to dewetting. Altogether, in most of the investigations on dewetting, annealing the film above the glass transition temperature of the polymer is a prerequisite for the nucleation to take place.

The relative surface chemical composition of the films was studied with X-ray photoelectron spectroscopy (XPS). Carbon with three bonds to oxygen is present only in CTA (binding energy 289.3 eV). Thus the O–C=O bond emission can be solely ascribed to the CTA component. Silicon is present in TMSC and also in the solid support, but considering the analysis depth of XPS, <10 nm, and the typical film thickness (20–80 nm), it is expected that all silicon arises from TMSC in the TMSC/CTA films. In Fig. 5 (top), the percentage of O–C=O bond emission is shown as a function of the fraction of CTA in the initial spin coating solution. With most blend ratios, the amount of a given component in the spin coating solution correlated with the amount of the same component present in the film, as has been found in studies with other polymer blends. However, ambiguity in XPS analyses is expected due to the non-homogeneous distribution of the components on the surface of the sample. It is apparent, nevertheless, that both horizontal and vertical phase separation took place during the film formation. The experimental points in Fig. 5 would be linearly aligned had the films exhibited only vertical phase separation. This is clearly not the case here and it also correlates with the observed phase separation patterns in Fig. 2. An interesting further observation from the XPS analysis is that TMSC seemed to be enriched on the surface, especially when applied as the majority phase (Fig. 5, bottom).

XPS results also allowed determination of substrate surface coverage by the film, as determined from the background signal. All untreated TMSC/CTA films and Cellulose/CTA films were closed films, in other words the films had no holes or pores that penetrated all the way down to the substrate. In Cellulose/- films, the blend ratios TMSC/CTA 1 : 2, 1 : 5 and 1 : 10 showed backgrounds typical for open, i.e., not fully covering, films (Fig. S3, ESI†). In these films, the residual cellulose layer did not cover the whole substrate. This could be due to the fact that in these blends the amount of TMSC was not enough (thin TMSC layer adjacent to the substrate) to sustain its shrinkage during conversion to cellulose. Alternatively, the TMSC layer did not fully cover the substrate.

To gain additional insight into the topmost molecular layer of the films, water contact angle (WCA) measurements were performed (Fig. 6). The contact angles of neat TMSC and CTA were 93 ± 1° and 58 ± 0.5° (standard deviation), respectively and they are in agreement with the values reported elsewhere. WCA of cellulose hydrolyzed from TMSC was 59 ± 1°. Such a high value can be explained by the roughness, crystallinity and morphology of the films and is the subject of ongoing studies.

The most striking result was that even a minor addition of TMSC to the spin coating solution caused the WCA of the
TMSC/CTA film to increase to a level of neat TMSC (Fig. 6). Thus, a critical, small amount of TMSC was enough to bring the WCA to a value similar to that of neat TMSC. As expected, the conversion of TMSC to cellulose reduced the WCA of the films. This is substantial indication that there is a thin TMSC top-layer on the films and it also correlates with the XPS results (Fig. 5).

Since TMSC apparently also formed the lower layer next to the substrate in the blend films (see the discussion in Fig. 2), a possible explanation for the presence of this overlayer is the occurrence of layer inversion\textsuperscript{32,39} which is subject to further speculation toward the end of this discussion.

After the second modification step, \textit{i.e.}, CTA dissolution, the contact angles stayed almost stable with respect to composition, close to the level of neat cellulose converted from TMSC. The slight variations were due to the fact that during selective dissolution there is always some CTA re-adsorption onto the cellulose surface.\textsuperscript{40} Roughness had only a minor effect on the WCA, the difference between the apparent WCA and WCA for an ideally smooth surface was within the standard deviation (Section S4, ESI\textsuperscript{†}).

Before putting forward a combined hypothesis to all aspects of the morphology formation, a summary of the main experimental observations is presented: (i) both vertical and horizontal phase separation took place (Fig. 2 and 5); (ii) concerning the vertical separation, TMSC formed a continuous layer next to the substrate (Fig. 2); (iii) a thin layer of TMSC prevailed also on the air-film interface with all blend ratios (Fig. 6); (iv) humidity and blend ratio played an important role in the morphology formation (Fig. 1 and 2); (v) pore growth was essentially linked to the CTA rich phase, but the presence of humid air was also vital (Fig. 1, 2 and 3); (vi) by increasing the fraction of CTA in the original spin coating solution, the surface density of pores increased (Fig. 4).

The vertical and horizontal phase separation into TMSC-rich and CTA-rich phases can be understood by the well-established transient bilayer theory (Scheme 1a and b, three topmost images).\textsuperscript{17} In short, the entropic optimization first induces vertical separation at the early stages of spin coating: a TMSC-rich layer forms next to the substrate surface while a CTA-rich layer is exposed on top. The occurrence of the TMSC-rich layer next to the SiO\textsubscript{x} substrate can be hypothetically ascribed to the presence of residual OH-groups in TMSC (\textit{C}/\textit{C}_2\textsubscript{4}/0.9 per monomer), resulting in strong affinity of the hydrophilic moieties in a hydrophobic solvent. Further, according to the transient bilayer theory, the upper CTA layer dewets after the vertical phase separation. The holes caused by dewetting are then filled by the still mobile TMSC-rich layer from underneath, resulting in laterally phase separated structures.\textsuperscript{16,17}

In the case of the intermediate blend ratios (TMSC/CTA 5 : 1–1 : 5), the apparent pore growth within the CTA-rich phase under humid atmosphere (Fig. 1 and 2) cannot be explained by
conventional transient bilayer theory. In general, there are two proposed routes to pore formation in polymeric films in the presence of humid air: breath figures and dewetting (Scheme 1). Breath figures have received far more extensive coverage in the literature. They are formed when evaporation of a high vapor-pressure solvent leads to cooling of the surface, which in turn enables the condensation of water from the ambient air (Scheme 1b). Water droplets nucleate, grow and sometimes coalesce on the surface and sink into the polymer solution while it is still mobile. After complete solvent and water removal, the porous and ordered imprint of the monodisperse water droplets on the film surface is exposed. In contrast to the observed, more arbitrarily scattered pores in the CTA phase (Fig. 2), however, breath figures are usually periodically aligned structures, formed by slow evaporation of the solvent and not by spin coating. In addition, the rims around the pores are generally absent from breath figures whereas they are a distinguishing feature of the pores formed by dewetting. Another feature promoting the dewetting route is the presence of the thin TMSC overlayer: several accounts demonstrate that during dewetting, the lower layer in a vertically phase separated system can partially or completely accumulate atop the upper layer as a continuous thin film (so-called layer inversion). Finally, a quantitative treatise by Hecht et al. on spin coating polymer film onto aluminium oxide substrate under humid atmosphere ruled out the possibility of breath figure formation as the reason for observed porous structures. The authors concluded that spin coating proceeds too fast for the metal oxide substrate to cool down sufficiently for breath figure formation.

For the aforementioned reasons, we favor dewetting as a hypothetical route to the pore formation in TMSC/CTA blend films (Scheme 1a). We emphasize again that the dewetting leading to pore formation in the CTA-rich phase is a different event to the dewetting occurring during the transient bilayer formation, described in the previous passage. Usually, dewetting that leads to pores occurs only upon annealing of spin coated films: the film is heated above the $T_g$ of a certain polymer and the more mobile polymer becomes unstable in the liquid state, resulting in pore formation. However, dewetting may also occur during spin coating, for example, when the films are very thin or when they are exposed to humidity. In the TMSC/CTA system, humidity may play a role as a plasticizer. The $T_g$ values of polysaccharides are known to undergo severe reductions when exposed to water or water vapor, and the reduced $T_g$ of CTA may facilitate its dewetting. The plasticization of CTA by water uptake is all the more likely because of its more hydrophilic nature in contrast to TMSC (see contact angle measurements in Fig. 6). In addition, the hypothetical presence of water at the interface between TMSC-rich and CTA-rich layers may reduce the energy barrier for the dewetting of the top CTA-rich layer. This would be analogous to the reported dewetting of a polymer film on top of an unoriented water film during spin coating. In addition to the humidity effect, $T_g$ is also reduced as a function of decreasing thickness in ultrathin films. However, the impact of thickness on $T_g$ is normally around 10%,
which is most likely overplayed by the humidity effect which can reduce the $T_c$ of polysaccharides by as much as 50%.

The final consideration in the hypothetical dewetting scenario (Scheme 1a) is layer inversion. When a vertically phase-separated bicomponent film strives to minimize its surface energy during dewetting, the material from the lower layer forms a continuous layer at the topmost surface. Similarly, upon dewetting the CTA-rich rim offers a site for layer inversion and the CTA-rich phase penetrates to the less viscous TMSC-rich layer. This again enables a part of the TMSC-rich phase to be transported to the air–polymer interface (Scheme 1a). Often the layer inversion reaches completion and the vertical phase separation is entirely inverted. Layer inversion occurs at a comparable rate with the competing dewetting phenomena, and in the rapid process of spin coating TMSC/CTA blends, both layer inversion and dewetting appear incomplete.

We emphasize that the favored scenario presented in Scheme 1a is merely a hypothesis. However, it does offer explanations to all features observed in the film: vertical and horizontal phase separation patterns according to the transient bilayer theory, pores surrounded by rims formed by dewetting, and the presence of a thin TMSC overlayer due to incomplete layer inversion occurring during dewetting.

Porous films from two hydrophobic polysaccharides offer interesting templates to materials science. Both TMSC and CTA can be readily hydrolyzed to cellulose, enabling a wide range of chemical modification steps available for cellulose. For example, glyco-modification of cellulose surfaces improves its bioactive response, which can facilitate, e.g., the biofunctional recognition properties via enhanced carbohydrate-protein interactions. Furthermore, the distinct swelling response of regenerated cellulose to water and water vapor can be utilized. Diagnostic applications, membrane technology, and catalytic use have the potential to benefit from the hierarchical length scales, chemical tunability, biological origin, and high surface area among other qualities of these films. We foresee that this fundamental survey of the unusual morphological versatility can serve as an important starting point for applying polysaccharide-based blend ultrathin films.

**Conclusions**

The construction of ultrathin bicomponent polysaccharide films with phase-specific pore formation was presented and the reasons behind genesis and evolution of morphology were scrutinized. The blend film morphology formation during spin coating was hypothesized to depend on various consecutive phenomena: vertical and lateral phase-separation occurring according to the transient bilayer theory, plasticization of the CTA phase under humid atmosphere leading to dewetting and phase-specific pore growth, and surface energy minimization which results in layer inversion during dewetting.

**Experimental**

**Materials**

Cellulose triacetate was obtained from Fluka and trimethylsilyl cellulose (TMSC) was synthesized and characterized as described previously. The weight average molecular weight and the number average molecular weight of TMSC were circa 231,000 and 83,000 g mol$^{-1}$, respectively, leading to a polydispersity index of 2.8. The degree of substitution according to XPS was 2.1. All solvents and other chemicals were of analytical grade and used as obtained from the manufacturer. Water used was of ultra-high quality purified with Millipore Direct-Q® 3 UV (Millipore, Molsheim, France). Untreated silicon wafers (Si 100 with native oxide layer on top, Okmetic, Vantaa, Finland) cut to ca. 1$\times$1 cm$^2$ squares were used as substrates.

**Spin coating**

Ultrathin films of TMSC and CTA blends were prepared with spin coating. TMSC and CTA were dissolved into chloroform with a solution concentration of 10 g dm$^{-3}$. Blends were prepared by mixing the two 10 g dm$^{-3}$ solutions and diluting the rest with chloroform in a way that the majority component concentration was always 5 g dm$^{-3}$ and the minority component concentration varied according to the TMSC/CTA ratio. The spin coater used was WS-650SX-6NPP/LITE (Laurell Technologies Corporation, North Wales, PA, USA). Before mounting the substrates on the spin coater, they were kept in the UV/ozonator for at least 20 minutes and prior to spin coating the blend solutions, bare substrates were rinsed twice with chloroform (4000 rpm for 10 s). Spin coating the blends was performed with the spinning speed of 4000 rpm and with the acceleration speed of 2130 rpm s$^{-1}$. The deposition of the blend solution was performed on a static substrate and the spinning was retained ca. 30 seconds after the disappearance of the Newtonian rings which usually took place during the acceleration. For spin coating under low-humidity conditions (RH = 15%), the spin coater chamber was carefully dried and flushed with nitrogen before mounting the substrate. For spin coating under higher humidity, water at different temperatures was introduced to the spinning chamber. The RH was monitored in situ with a probe (testo 625, Brandt Instruments, Prairieville, LA) above the substrate.

**Selective conversion and dissolution**

The spin coated films containing TMSC were hydrolyzed in a 2 M aqueous HCl vapor environment under vacuum for 2 minutes. During the hydrolysis, TMSC is converted back to cellulose thus the TMSC patches contract due to the replacement of the bulky trimethylsilyl groups with tightly packed hydroxyl groups (Chart 1). As cellulose does not dissolve in common solvents, it was possible to selectively dissolve the remaining CTA with chloroform. The dissolution was performed by immersing the supported films in excess chloroform for 1 h with occasional stirring. Afterward, the wafers were rinsed with ~50 ml of fresh chloroform.

**Atomic force microscopy (AFM)**

Film surface morphology and layer thickness was determined using a Nanoscope IIIa Multimode scanning probe microscope (Digital Instruments Inc., Santa Barbara, CA, USA). The images were scanned in tapping mode with a J-scanner and silicon cantilevers (NSC15/AIBS from Ultrasharp, μ-Masch, Tallinn, Estonia). The radius of curvature for the tip according to the manufacturer was less than 10 nm and the typical resonance
frequency of the cantilever was 325 kHz. Two parallel surfaces were prepared and at least two points on each were imaged. No image processing besides flattening was performed. Film thickness was studied by scratching the samples with a needle and determining the height difference between the revealed substrate and the intact areas of the film. All quantitative data were extracted from the height images.

Image analysis

Image analysis was performed using Nanoscope (version V6.13 R1, Digital Instruments Inc., Santa Barbara, CA, USA), Nanoscope Analysis (version 1.20, Veeco, Plainview, NY, USA) and Scanning Probe Image Processor (SPIP) (version 4.5.3, Image Metrology, Lyngby, Denmark) softwares. The pore surface coverage was determined using the Grain Analysis module in SPIP with Threshold algorithm.

X-Ray photoelectron spectroscopy (XPS)

Chemistry of the film surfaces was studied with XPS. The measurements were performed with an AXIS 165 (Kratos Analytical, Manchester, UK) spectrometer using a monochromated Al Kα X-ray source. All samples were pre-evacuated overnight to stabilize ultra-high vacuum (UHV) conditions. UHV condition was monitored throughout the measurement. Two parallel samples were prepared and each sample was analyzed at least at three points. Elemental surface composition was determined from low resolution scans recorded with 80 eV pass energy and 1 eV steps. Carbon 1s and oxygen 1s high resolution spectra were determined using 20 eV pass energy at 0.1 eV steps. The carbon 1s emission was resolved into various contributions corresponding to distinct chemical states of carbon according to the literature. The degree of substitution (DS) of TMSC was calculated from XPS measurements. DS of TMSC was 2.1, which means that 2.1 of the three hydroxyl groups in the repeating unit of cellulose were replaced by trimethylsilyl groups during the TMSC synthesis.

Contact angle measurements

Contact angle measurements with water were performed with CAM-200 contact angle goniometer (KSV Instruments Ltd, Helsinki, Finland). The measurements were conducted in ambient air at room temperature. The size of the water droplet was 6.7 μl. At least five measurements from two different surfaces per test point were performed. Contact angle calculations were performed with the CAM-200 software (KSV Instruments Ltd, Helsinki, Finland). The calculations are based on a numerical solution of the full Young–Laplace equation.

Acknowledgements

We acknowledge Dr Joseph Campbell and Dr Leena-Sisko Johansson for recording the XPS data and helping in analyzing the results. EK acknowledges Academy of Finland (no. 129068) for financial support.
Notes and references


Electronic Supplementary Information

for

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

by

Laura Taajamaa, Orlando Rojas,* Janne Laine, Eero Kontturi*

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).
**Figure S2.** $5 \times 5 \mu m^2$ 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. 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 the Wenzel equation:

\[
\cos \theta^* = r \cos \theta
\]  

(S1)

Where \( \theta^* \) 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 \( \theta \) 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.

![Surface roughness graph](image)

**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 guide the eye.

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

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

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References
