Utilizing Polymer Blends to Prepare Ultrathin Films with Diverse Cellulose Textures

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Summary: This paper presents an overview of the recent work on ultrathin polymer blend films containing cellulose. Three systems prepared via trimethylsilyl cellulose derivative, which is subsequently hydrolyzed to cellulose, are presented: polystyrene/cellulose, poly(methyl methacrylate)/cellulose and polystyrene-*block*-polyethyleneoxide/cellulose. Diverse textures emerge within the films depending on the interactions between the polymers and their interactions with the substrate as well as on different solubilities of the polymers. Furthermore, an ultrathin film containing a cellulose/xylan blend is presented. This film was deposited directly from a common solvent (dimethylacetamide/lithium chloride) and it did not exhibit distinct morphological patterns comparable to the blends with synthetic polymers.

Keywords: atomic force microscopy (AFM); blends; cellulose; phase separation; ultrathin films

Introduction

Blending two or several polymers together may lead to material properties that exceed those of a single polymer.[1] Therefore, applied and fundamental research has extensively been performed on polymer blends in bulk,[1,2] including cellulose-containing blends.[3] Once a blend of immiscible polymers is subjected to geometrical constraints, on the other hand, the occurring phase separation is influenced by the presence of an interface.[4] The resulting morphologies are very distinct and they have been subject to intense research activities during the past 15 years.[4–12] Despite this, almost no literature accounts exist for ultrathin films of blends containing cellulose, which has probably been caused by its immiscibility in common solvents.[13] When the interfacial behavior of polymer blends is investigated, the polymers are usually dissolved in a common solvent and an ultrathin film of the mixture is cast on a solid substrate by removing the solvent with spin coating technique. The limited amount of solvents for cellulose has hindered the opportunities to perform such research on blends containing cellulose and synthetic polymers.

We have circumvented the solubility issues by applying a dissolving derivative of cellulose: Trimethylsilyl cellulose (TMSC) can be dissolved in any common hydrophobic solvent. In addition, TMSC is easy to hydrolyze to cellulose by vapor phase acid in such manner that the morphology of the already cast film remains largely intact.[14–16] To summarize the approach, TMSC has been dissolved in a common hydrophobic solvent with a synthetic (hydrophobic) polymer, the mixture has been cast as an ultrathin film by spin coating, and the TMSC in the film has then been hydrolyzed to cellulose by acid vapor, resulting in a blend film with cellulose and an additional polymer.

Besides extensive fundamental research, ultrathin films of polymer blends have found applications in such areas as antireflective coatings,[17] and light emitting diodes[18] among others. By introducing cellulose to ultrathin blend films, we hope

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to bring in a novel aspect which employs the peculiar properties of the most abundant biopolymer. Moreover, the possibility to prepare varied, tunable textures of cellulose is likely to enable a more diverse usage of model films which is a recently popular form of exploitation of ultrathin cellulose films.[19] In this paper, we will present a brief overview of the fundamental work concerning the preparation of ultrathin blend films that contain cellulose. These include the already published studies with polystyrene[20,21] and poly(methyl methacrylate)[22] as well as unpublished results with a common amphiphilic block copolymer and a cellulose/xylan system. In this latter case, cellulose and xylan have been directly dissolved in a common solvent (LiCl in dimethylacetamide) without the usage of a dissolving cellulose derivative. Although some of the work presented in this paper has already been published, the aspect of utilizing different binary blend systems to prepare diverse cellulose textures cannot be perceived from the individual publications.

Experimental Part

Materials

Trimethylsilyl cellulose (TMSC) was synthesized from Cellulose powder from spruce (Fluka) according to reference.[16] Polystyrene (PS) ($M_W = 2.8 \times 10^5$ Da) and poly(methyl methacrylate) (PMMA) ($M_W = 1.2 \times 10^5$ Da) were purchased from Aldrich. Polystyrene(29800 Da)-*block*-polyethylene oxide(8400 Da) (PS-*b*-PEO) was obtained from Polymer Source. Cellulose (powder from spruce) was supplied by Fluka Chemica and xylan (from birch, containing ca. 10% of α-D-methylglucuronic acid side groups) by Fluka BioChemica. The water soluble fraction of xylan was removed by immersing it in Milli-Q water and separating the solid residue by centrifuging. Toluene and dimethylacetamide (DMAc) were p.a. grade from Aldrich. Lithium chloride (LiCl) was purchased from Fluka in anhydrous form. Single crystal silicon (Si <100>) wafers with native oxide layer on top were supplied by Okmetic (Espoo, Finland).

Preparation of Blend Films of Cellulose and Synthetic Polymers

Toluene solutions of TMSC, PS, PMMA and PS-*b*-PEO were prepared in 10 g dm^{-3} concentration. Blend solutions were prepared by mixing the two 10 g dm^{-3} solutions and diluting the resulting solution with toluene so that the concentration of the majority phase polymer was always 5 g dm^{-3}. This concentration in the spin coating solution results in a film of ca. 10-20 nm thickness as described in our previous papers on TMSC blends.[20–22] The solutions were spin coated on untreated silicon wafers at 4000 rpm (acceleration 2100 rpm/s). Prior to spin coating, the silicon substrates were rinsed twice with toluene (4000 rpm, ~15 s). The deposition of the blend solution was performed on a static substrate, the spinning was retained for ~30 s after the disappearance of the Newtonian rings, which signals that the solvent evaporation has reached conclusion. After deposition, the film was exposed to 2M HCl atmosphere and retained there for 2 minutes. This treatment is enough to hydrolyze TMSC to cellulose.[16]

Preparation of Cellulose/Xylan Blend Films

Cellulose and xylan were dissolved in dimethylacetamide with 8% (w/w) LiCl following a solvent exchange with water, methanol and dimethylacetamide as described by McCormick et al.[23] Blend solutions were prepared by mixing the two 10 g dm^{-3} solutions and diluting the resulting solution with DMAc/LiCl so that the concentration of the majority phase polymer was always 5 g dm^{-3}. The solutions were spin coated on untreated silicon wafers at 4000 rpm (acceleration 2100 rpm/s). Prior to spin coating, the silicon substrates were rinsed twice with pure dimethylacetamide (4000 rpm, ~15 s). The deposition of the blend solution was performed on a static substrate, the spinning was retained for ~30 s after the

disappearance of the Newtonian rings, which signals that the solvent evaporation has reached conclusion. After the deposition, the films were treated at 100 °C for 30 min. After the films had cooled down to room temperature, they were washed with copious amounts of water in order to remove the LiCl. The films were then blow-dried with dry nitrogen gas and further dried in 150 °C for 60 min to ensure that excess DMAc was evaporated.

Atomic Force Microscopy (AFM) was performed with a Nanoscope IIIa Multimode scanning probe microscope (Digital Instruments Inc., Santa Barbara, CA) equipped with J scanner. The images were scanned in tapping mode with NSC15/AIBS tips (Ultrasharp μmasch, Tallinn, Estonia).

Results and Discussion

Blend Films of Cellulose and Synthetic Polymers

The morphology development of the binary polymer blend system during spin coating can be explained by the transitive bilayer theory, originally proposed by Walheim et al.[6] and verified by Heriot and Jones.[24] First two phases form vertically with respect to the substrate, each enriched in one polymer. As spin coating proceeds further, the upper layer dewets. Holes are formed and these holes are subsequently filled with the polymer from the lower layer, resulting in lateral phase separation patterns.

Figure 1 depicts a schematic representation of how the final morphology of the cellulose/synthetic polymer blend films is achieved. First, the TMSC/synthetic polymer blend is spin coated from a solution to the substrate and lateral phase separation occurs (Figure 1a and 1c). Second, the TMSC is hydrolyzed to cellulose with gaseous hydrochloric acid, vaporized from an aqueous solution of 2 M HCl (Figure 1b and 1d). The hydrolysis has been shown to proceed to full extent, i.e., TMSC is completely transformed to cellulose and the volatile side products diffuse out of the film and evaporate, leaving behind a pristine cellulose film.[14–16] The synthetic polymers used in this study (PS, PMMA, and PS-b-PEO) remain unaffected by the acid treatment. When planning further combinations with synthetic polymers,

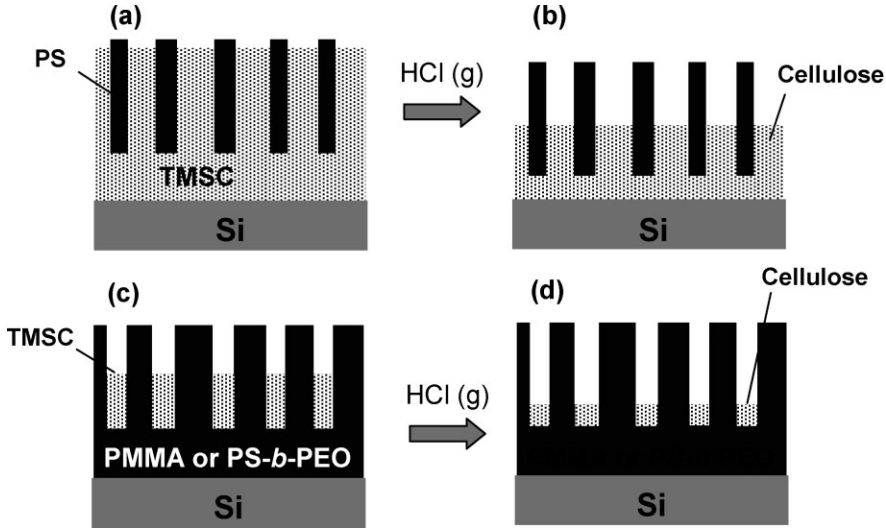

Figure 1.
Schematics of the cross-sections of blend films: (a,c) TMSC laterally phase separates with the synthetic polymer and (b,d) TMSC is readily hydrolyzed to cellulose, resulting in contraction of that phase. The synthetic polymer stays intact in the process.

one has to bear in mind that a number of polymers, such as polyesters, are not inert in acidic atmosphere.

Figure 2 shows the actual morphological details of the cellulose/synthetic polymer blends in representative $10 \times 10\ \mu m^2$ AFM images. Figure 2a and 2b are both examples of cellulose/PS blends. When the cellulose/PS ratios are close to each other, PS forms a bicontinuous network on top of a continuous cellulose matrix (Figure 2a).[20] Intriguingly, when the relative amount of PS is reduced, it contracts to droplets (Figure 2b).[21] The droplet formation occurs because dewetting during spin coating can proceed further with smaller initial amounts of PS.[21]

These droplets are circular in the radial cross section but very flat in vertical dimension, meaning that PS is present as disk-like agglomerates on the cellulose surface. The size of the PS disks can be tuned from hundreds of nanometers down to nanometer dimensions in a highly reproducible fashion just by tuning the initial TMSC/PS ratio in the spin coating solution. Because PS is a distinctively hydrophobic structure, the tunable size of the PS disks implies that the hydrophobicity of the cellulose films can be adjusted by this method.[21]

In more general terms, one could envisage that blending any different hydrophobic polymer with TMSC can lead to a cellulose film with different chemical properties.

By blending TMSC with polymers that have different chemical structures, different functionalities are easy to introduce on the cellulose film surface just by spin coating the mixture and hydrolyzing the TMSC to cellulose. Droplet formation as the final stage of dewetting has also been utilized with the PMMA/cellulose blend films (Figure 2c).[22] However, in this case PMMA forms the majority phase – in contrast to cellulose forming the majority phase in the case of PS blends. When considering the transient bilayer theory, PMMA has formed the lower layer close to the substrate in the early stages of spin coating. It is the TMSC layer that collapses to droplets on top of PMMA. Curiously, TMSC appears to form cavities on the PMMA layer upon its collapse (Figure 2c, see also the schematics in Figure 1c and 1d). The cavity formation can be explained by the different solubility of the two polymers in the spin coating solvent (toluene).[6] TMSC is more soluble in toluene, which means that the solvent stays longer in the TMSC phase during the spin coating. In the final stages, when the solvent is finally removed from the TMSC droplets, they rapidly sink in and form the cavities on PMMA. These sunken droplets inside the

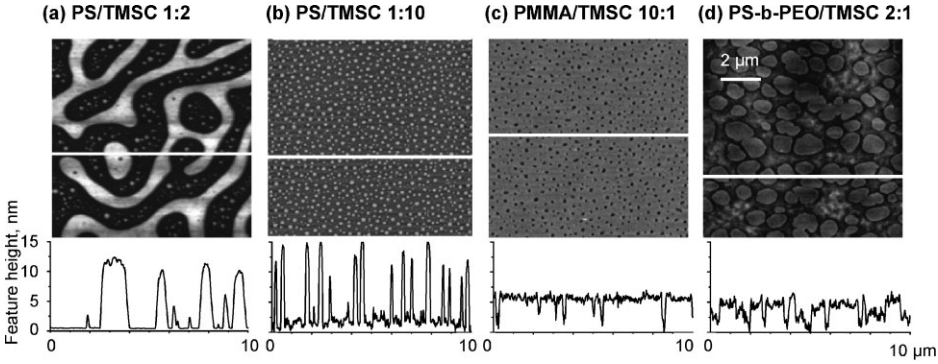

Figure 2.

$10 \times 10\ \mu m^2$ AFM height images of (a) PS/cellulose blend film with original PS/TMSC ratio of 1:2, (b) PS/cellulose blend film with original PS/TMSC ratio of 1:10, (c) PMMA/cellulose films with original PMMA/TMSC ratio of 10:1, and (d) PS-b-PEO/cellulose blend film with original PS-b-PEO/TMSC ratio of 2:1. Representative height profiles are presented under each image. A white line in the images denotes the location of the height profile.

lower majority phase have been reported previously with synthetic polymers.[25] Upon hydrolysis of TMSC to cellulose, the phase in the bottom of the cavities shrinks even lower (Figure 1c–1d). The final result is a PMMA film with nanometer sized cavities which have small disks of cellulose embedded on the bottom of the cavities.

Figure 2d illustrates the morphology of a cellulose/PS-*b*-PEO blend. Arbitrarily shaped disk-like structures represent the PS-*b*-PEO phase whereas the TMSC phase forms the bicontinuous network in between the disks. It is evident that the disk-like structures consist of PS-*b*-PEO because of the cylindrical patterns which are particularly conspicuous in the higher magnification images (not shown). The cylinders are a result of nano-scale segregation of the two immiscible blocks and their formation has been extensively reported in the literature.[26] Similar phase separation applies to the TMSC/PS-*b*-PEO films as the one already discussed for TMSC/PMMA system: PS-*b*-PEO forms the lower layer whereas TMSC forms the top layer. However, the cellulose layer is actually on a lower level than the surface of the underlying PS-*b*-PEO layer (see the cross-sectional schematics of Figure 1c and 1d). This behavior can be attributed again to the different solubility properties of the spin coated polymers, which was already discussed in the previous paragraph.[6]

Blend Films of Cellulose and Xylan

Figure 3 exposes the AFM images of cellulose/xylan blends spin coated from DMAc/LiCl solvent. The lack of morphological contrast between the different cellulose/xylan ratios is striking. The conclusion is that no lateral phase separation has taken place between cellulose and xylan. We emphasize that the water soluble fraction has been removed from the xylan prior to its dissolving in DMAc/LiCl. This prevents the removal of xylan during the washing step after spin coating – something that was also clarified by spin coating a film of (water extracted) xylan only. A film was clearly present after the washing step (results not shown).

We propose two possible reasons for the lack of morphological contrast in cellulose/xylan blend films: (i) cellulose and xylan exist as miscible complexes in DMAc/LiCl or (ii) xylan does not dissolve properly in DMAc/LiCl. The first alternative is a possibility because the phase separation requires immiscibility of the polymer. The second alternative is plausible because it

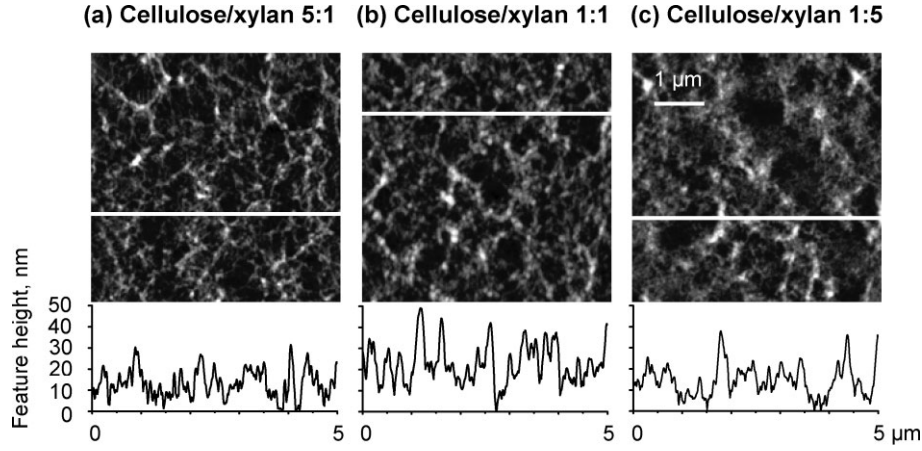

Figure 3.
$5 \times 5\ \mu m^2$ AFM height images of cellulose/xylan blend films spin coated from DMAc/LiCl. Cellulose/xylan ratios are (a) 5:1, (b) 1:1, and (c) 1:5. Representative height profiles are presented under each image. A white line in the images denotes the location of the height profile.

would no longer be a polymer blend system but a mixture of a dissolved polymer (cellulose) and a colloidal dispersion (xylan). However, these alternatives are purely speculative and based on preliminary results only (although the AFM images were reproducible on different spots on the film and on parallel samples). Further experiments are currently underway to validate the reason behind the absence of phase separation.

Conclusion

We have shown that blending trimethylsilyl cellulose (TMSC) with various synthetic hydrophobic polymers in a common solvent is a facile method to prepare ultrathin films of cellulose coexisting with other polymers with clearly phase separated structures. The method can be utilized to, for instance, prepare cellulose films with different chemical functionalities. It is also a viable tool for fabrication of synthetic polymer surfaces with various cellulose textures, as exemplified by PMMA films with nanometer sized cavities bearing cellulose disks on the bottom of the cavities. On the other hand, blending cellulose and xylan directly in a common solvent (DMAc/LiCl) did not lead to phase separation. The reasons behind the absence of phase separation remained unclear.

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