STABILITY AND INTERFACE PROPERTIES OF THIN CELLULOSE ESTER FILMS ADSORBED FROM ACETONE AND ETHYL ACETATE SOLUTIONS

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Stability and interface properties of cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) films adsorbed from acetone or ethyl acetate onto Si wafers have been investigated by means of contact angle measurements and atomic force microscopy (AFM). Surface energy ($\gamma_{S\text{ total}}$) values determined for CAP adsorbed from acetone are larger than those from ethyl acetate. In the case of CAB films adsorbed from ethyl acetate and acetone were similar. Dewetting was observed by AFM only for CAP films prepared from ethyl acetate, corroborating with positive values of effective Hamaker constant found only for this system. Sum frequency generation (SFG) vibrational spectra indicated that CAP and CAB films prepared from ethyl acetate present more alkyl groups oriented perpendicularly to the polymer-air interface than those films prepared from acetone. Such preferential orientation corroborates with macroscopic contact angle measurements. Moreover, SFG spectra showed that acetone binds strongly to Si wafers, creating a new surface for CAP and CAB films.

Keywords: cellulose ester, films, dewetting, atomic force microscopy, sum frequency generation.

Introduction

Thin polymeric films are largely used in many technological applications, as for instance, as coatings, paint, and sensors. In such situations, stable, continuous and homogeneous layers are required. Polymer surface energy and interface tension between substrate and polymeric film drive the stability of thin polymeric films. If the work of cohesion is larger than the work of adhesion, thin polymer film becomes unstable, resulting in the dewetting phenomena [1,2]. However, the solvents used for film preparation might also affect structure, wettability and stability of thin polymeric films. Special attention has been devoted to the effect of solvent used for spin-coating polymer films on the resulting surface properties [3-9]. Not only the evaporation rate of the solvent plays a very important role on the spin-coated [3-9] or cast film [10] uniformity, but also solvent quality and the balance between substrate-polymer interaction and substrate-solvent interaction [7-9,11]. Nevertheless, there are scarce studies on the effect of solvent on the stability and surface properties of ultrathin (d < 5 nm) adsorbed polymer films.

Cellulose esters are frequently applied as binders, additives, film formers or modifiers in automotive, wood, plastic and leather coatings applications [12]. Cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) find place in the coating industry because they reduce dry time, improve flow and leveling, control viscosity and gloss, are stable carriers for metallic pigments, improve UV stability and reduce plasticizer migration, among many other benefits [12].
Moreover, cellulose esters films also proved to be efficient supports for adsorption of proteins [13,14] and cell growth [15]. In this work, surface properties and stability of CAP and CAB ultrathin films adsorbed from acetone or ethyl acetate solutions onto Si wafers, when they are heated above their glass transition temperature, has been investigated. Acetone and ethyl acetate are good solvents for CAP and CAB [9]. Surface properties have been determined for adsorbed CAP and CAB films by means of contact angle measurements. Film stability was predicted with basis on thermodynamic parameters and compared with atomic force microscopy (AFM) analyses. Sum frequency generation (SFG) vibrational spectroscopy, a sensitive tool for interfacial analyses, was used to gain insight about molecular orientation at polymer/substrate and solvent/substrate interfaces.

**Experimental**

*Materials*

Silicon wafers (100) purchased from Silicon Quest (California, USA) with native oxide layer approximately 2 nm thick were used as substrates. They were cut in small pieces of (1.0 x 1.0) cm², rinsed in a standard manner [16], dried under a stream of N₂ and characterized prior to use. Cellulose acetate propionate and cellulose acetate butyrate (powders free of plasticizer) were kindly supplied by Eastman Chemical Co., Brazil. Analytical grade acetone and ethyl acetate were used to prepare the solutions at the polymer concentration of 5 mg/mL.

*Preparation of cellulose ester films.* Silicon wafers were dipped into homogeneous solutions of CAP and CAB prepared in acetone or ethyl acetate at 5 mg mL⁻¹ at (24 ± 1) °C. After 21 hours they were removed from the solutions, washed with pure acetone or ethyl acetate and dried under a stream of N₂. The samples were annealed at 170°C under reduced pressure (60 mm Hg) during 4, 15, 60 and 168 hours.

*Ellipsometry.* Ellipsometric measurements were performed in the air using a vertical computer-controlled DRE-EL02 ellipsometer (Ratzeburg, Germany). The angle of incidence was set at 70.0° and the wavelength, λ, of the He-Ne laser was 632.8 nm. For the data interpretation, a multilayer model composed by the substrate, the unknown layer and the surrounding medium should be used. Then the thickness (dₓ) and refractive index (nₓ) of the unknown layer can be calculated from the ellipsometric angles, Δ and Ψ, using the fundamental ellipsometric equation and iterative calculations with Jones matrices [17].

*Contact angle measurements* were performed at (24 ± 1) °C in a home-built apparatus [18]. In order to investigate the effect of solvent used on the surface energy of adsorbed film, measurements were performed for CAP or CAB films adsorbed from ethyl acetate or acetone solutions (5 mg/mL). The
surface energy of the polymers was determined indirectly using contact angle measurements performed either with diiodomethane > 99.5% (purely dispersive nature) and water as described elsewhere [18-21]. Sessile drops of 8 μL were used for the $\theta_{\text{diiodomethane}}$ and $\theta_{\text{water}}$. At least three samples of the same composition were analyzed for each test liquid.

*Atomic Force Microscopy (AFM)* measurements were performed in a PICO SPM-LE (Molecular Imaging) microscope in the intermittent contact in air at room temperature, using silicon cantilevers with resonance frequency close to 300 kHz. Scan areas varying from (5x5) μm$^2$ to (1x1) μm$^2$ with a resolution of 512 x 512 pixels were obtained. Image processing and the determination of the root mean square (rms) were performed using the Pico Scan software. Mean roughness value (rms) is calculated as the root mean square value of all peak-to-valley distances measured over the scanned area after surface flattening, where the software subtracts linear fit from data. At least two films of the same composition were analyzed at different areas of the surface before and after annealing.

*Sum frequency generation (SFG)* [22] vibrational spectra were obtained with a commercial SFG spectrometer (Ekspla, Lithuania) equipped with a pulsed Nd+:YAG laser at 1064 nm (28 ps pulse duration, 20 Hz repetition rate) and harmonic unit generating second and third harmonics (532 and 355 nm, respectively). The first is the visible beam that excites the sample (pulse energy ~ 950 μJ). The third harmonic and fundamental beams pump an optical parametric amplifier with a difference-frequency stage that generates an infrared (IR) beam tunable from 1000 to 4000 cm$^{-1}$ (pulse energy ~30-150 μJ), which overlaps the visible beam on the sample. The incidence angles and approximate spot sizes on the sample are 51°, 500 μm and 60°, 1000 μm for the IR and visible beams, respectively. The sum-frequency signal as a function of IR frequency is collected by a photomultiplier after spatial and spectral filtering. For each scan, data are collected with 100 shots/data point in 3 cm$^{-1}$ increments typically during 8 minutes. SFG spectra were obtained with ssp polarization combination, where s and p stand for polarized light perpendicular and parallel to the surface, respectively, and the first s, second s, and last p represent the polarizations of SFG, visible, and infrared light, respectively. CAP and CAB films adsorbed onto quartz (SiO$_2$) slides either from acetone or ethyl acetate solutions at 5 mg mL$^{-1}$ and (24 ± 1)°C. After 21 hours slides were removed from the solutions, washed with pure acetone or ethyl acetate and dried under a stream of N$_2$. After that spectra were obtained in air. For *in situ* measurements at (24 ± 1)°C, quartz slide was arranged inside the fluid cell, which was filled up either with acetone or ethyl acetate.
Results and discussion

The mean thickness values determined in air for CAP and CAB films obtained from acetone amounted to \((2.1 \pm 0.9) \text{ nm}\) and \((1.9 \pm 0.3) \text{ nm}\), respectively, and from ethyl acetate they were \((1.3 \pm 0.3) \text{ nm}\) and \((0.9 \pm 0.2) \text{ nm}\), respectively. Considering that a cellulose monolayer is \(\sim 0.7 \text{ nm}\) thick [23]. Adsorbed layers stemming from acetone solution were thicker than those from ethyl acetate. The same tendency was observed for spin-coated CAP and CAB films when acetone or ethyl acetate was used as solvents [9]. Two factors might explain this behavior: (i) acetone is more volatile than ethyl acetate, leading to thicker films [3-9] and (ii) the more favorable acid-base interaction for \(\text{SiO}_2/\text{acetone}\) (+ 18 RT) than for \(\text{SiO}_2/\text{ethyl acetate}\) (+ 24 RT) [24], so that acetone evaporation is not complete, resulting in thicker polymer films.

AFM topographic images obtained for CAP films adsorbed onto silicon wafers from acetone after annealing (images not shown) indicate very smooth surfaces. These films are very stable even after 168 hours annealing; no significant changes in mean thickness or roughness values could be observed. CAP films adsorbed from ethyl acetate solutions were very smooth (Figure 1a). However, upon annealing dewetting structural features (rims and mean roughness increase) appeared on the surface (Figure 1b). Regardless the solvent used for adsorption of CAB onto Si wafers, films were very smooth and stable, as evidenced by AFM topographic images (images not shown), even after one week annealing.

![Figure 1](image1.png)

Figure 1. AFM images \((1\times1)\mu\text{m}^2\) obtained in air for CAP adsorbed from ethyl acetate solutions \((5\text{mg/mL})\) onto Si wafers: (a) just after preparation \((\text{rms} = 0.46 \text{ nm})\) and (b) after 60 h annealing \((\text{rms} = 0.74 \text{ nm})\).

The stability of polymeric films depends on polymer and substrate surface energies. The surface tension \(\gamma\) of a material can be considered as the sum of the dispersive \(\gamma_{S}^{d}\) and polar \(\gamma_{S}^{p}\) components [25]. From \(\gamma_{S}^{d}\) it is possible to calculate the Hamaker constant for the polymer/polymer attraction \(A_{\text{poly/poly}}\) [26]:

\[
(\gamma_{S}^{d})^{2} 24\pi d^{2} = A_{\text{poly/poly}} \quad (1)
\]
where \(d\) (\(d \approx 1.6\) Å) is the distance between two atoms [19].

The difference between Hamaker constant values for the polymer/polymer attraction (\(A_{\text{poly/poly}}\)) and polymer/substrate interaction (\(A_{\text{poly/substrate}}\)) yields the effective Hamaker constant (\(A_{\text{eff}}\)). If \(A_{\text{eff}}\) is positive, fluctuations in film thickness are expected, and after a characteristic time, the film will rupture [2]. Negative values for \(A_{\text{eff}}\) indicate long range apolar van der Waals repulsion, which promotes film stability and wetting [1,2]. \(A_{\text{poly/substrate}}\) can be calculated by Lifshitz-van der Waals equation [27]. \(A_{\text{poly/poly}}\) also can be calculated from equation 1, if \(\gamma_{Sd}\) value is known. Combining Young’s equation [28] and harmonic mean equation one can calculate \(\gamma_{Sd}\) value from experimental contact angle data [29].

If contact angles measurements are performed with drops of at least two liquids of known \(\gamma_{LV}^d\) and \(\gamma_{LV}^p\) onto polymer surface, it is possible to calculate the dispersive \(\gamma_{Sd}\) and polar \(\gamma_{Sp}\) components of polymer surface. Such equations are defined for smooth, rigid, chemically homogeneous, insoluble and non-reactive polymer surfaces. AFM images evidenced smooth CAP and CAB films adsorbed onto Si wafers either form acetone or ethyl acetate solutions, thus contact angle \(\theta\) measurements were performed with drops of water and diiodomethane, as presented in Table 1. Comparing \(\theta\) values obtained for water (highest polarity) drops on CAP films adsorbed from acetone (30°) and ethyl acetate (48°), one notices a difference of 18°, which indicates that in the former surfaces are more hydrophilic than in the latter. The same behavior was also observed for CAB films, with difference of 8°. \(\theta\) values obtained for diiodomethane (apolar) drops on CAP or CAB films were smaller when the solvent used was ethyl acetate, indicating that ethyl acetate induced the formation of more hydrophobic films.

\(A_{\text{poly/poly}}\) and \(A_{\text{eff}}\) values were calculated (Table 1). \(A_{\text{poly/poly}}\) are larger for CAP and CAB films adsorbed from ethyl acetate than from acetone. Regardless the model used for calculation of dispersive \(\gamma_{Sd}\) component, positive \(A_{\text{eff}}\) value indicative of film instability was observed for CAP films adsorbed from ethyl acetate. In fact, AFM images in Figure 1 evidenced dewetting only for annealed CAP films adsorbed from ethyl acetate. These findings are very important because they reveal that thin films stability depends not only on the polymer surface and substrate properties but also on the solvent used for film preparation. Moreover, \(\gamma_{Sd}\) and \(A_{\text{poly/poly}}\) values calculated with harmonic model were larger than those determined with geometric model, indicating that prediction of film stability might be model dependent.

Regardless the model used for calculation of surface energy \(\gamma_{S\text{total}}\) values determined for CAP adsorbed from acetone are larger than those from ethyl acetate, mainly because \(\gamma_{Sp}\) contribution for films from acetone is much larger than that for films from ethyl acetate. The same tendency was observed for CAB films. However, \(\gamma_{S\text{total}}\) values determined for CAB films are
smaller than those found for CAP films adsorbed from the same solvent. A similar behavior was recently reported for a series of cellulose esters [20]. The main reason for this effect is surface energy decrease with the increase of alkyl ester group size, which weakens van der Waals interactions.

Table 1: Advancing contact angle measurements for CAP and CAB adsorbed from acetone or ethyl acetate solutions (5mg/mL) onto Si wafers using drops of diiodomethane (θ_{Diiodomethane}) and water (θ_{Water}) as test liquids. Dispersive (γ^d) and polar (γ^p) components values of the surface tension determined by harmonic model (hm) and geometric model (gm). Effective Hamaker constant A_{eff} is the difference between A_{poly/poly} and A_{poly/substrate}, which was calculated as 6.5 x 10^{-20} J (see Ref. 30).

<table>
<thead>
<tr>
<th>Sample</th>
<th>θ_{Diiodomethane} (°)</th>
<th>θ_{Water} (°)</th>
<th>γ^d (mJ/m²)</th>
<th>γ^p (mJ/m²)</th>
<th>γ_{total} (mJ/m²)</th>
<th>A_{poly/poly} x 10^{-20} (J)</th>
<th>A_{eff} x 10^{-20} (J)</th>
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<tbody>
<tr>
<td>CAP</td>
<td>52 ± 1</td>
<td>30 ± 1</td>
<td>34.9 ± 0.3</td>
<td>34.3 ± 0.3</td>
<td>69.2 ± 0.4</td>
<td>6.7 ± 0.1</td>
<td>+0.2 ± 0.1</td>
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<td></td>
<td>(hm)</td>
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<tr>
<td></td>
<td>33.2 ± 0.3</td>
<td>33.0 ± 0.3</td>
<td>66.2 ± 0.3</td>
<td>64.4 ± 0.1</td>
<td></td>
<td></td>
<td>-0.1 ± 0.1 (gm)</td>
</tr>
<tr>
<td>(EA)</td>
<td>45 ± 2</td>
<td>48 ± 1</td>
<td>37.8 ± 0.4</td>
<td>24.5 ± 0.2</td>
<td>62.3 ± 0.4</td>
<td>7.3 ± 0.1</td>
<td>+0.8 ± 0.1</td>
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<td></td>
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<tr>
<td></td>
<td>37.0 ± 0.4</td>
<td>20.5 ± 0.2</td>
<td>57.5 ± 0.4</td>
<td>7.1 ± 0.1</td>
<td></td>
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<td>+0.6 ± 0.1</td>
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<td></td>
<td>(gm)</td>
<td>(gm)</td>
<td>(gm)</td>
<td>(gm)</td>
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<tr>
<td>CAB</td>
<td>56 ± 2</td>
<td>42 ± 2</td>
<td>32.4 ± 0.3</td>
<td>29.5 ± 0.3</td>
<td>61.9 ± 0.4</td>
<td>6.3 ± 0.1</td>
<td>-0.2 ± 0.1 (hm)</td>
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<td>(hm)</td>
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<tr>
<td></td>
<td>30.9 ± 0.3</td>
<td>27.6 ± 0.3</td>
<td>58.5 ± 0.4</td>
<td>6.0 ± 0.1</td>
<td></td>
<td></td>
<td>-0.5 ± 0.1 (gm)</td>
</tr>
<tr>
<td>(A)</td>
<td>51 ± 1</td>
<td>50 ± 1</td>
<td>34.9 ± 0.3</td>
<td>24.3 ± 0.2</td>
<td>59.2 ± 0.4</td>
<td>6.7 ± 0.1</td>
<td>+0.2 ± 0.1</td>
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<td></td>
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<td></td>
<td>33.7 ± 0.3</td>
<td>21.0 ± 0.2</td>
<td>54.7 ± 0.4</td>
<td>6.5 ± 0.1</td>
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<td>0 (gm)</td>
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<td>(EA)</td>
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SFG is a second-order nonlinear optical process, where electric-dipole in a bulk with inversion symmetry is forbidden, but it is allowed at interfaces because inversion symmetry is broken [22, 31-33]. Therefore, it is sensitive to the interfacial structure between two centrosymmetric media. Moreover, input/output polarization dependence of the spectra provides information about average orientation of molecules at surfaces. SFG vibrational spectra were obtained in order to understand the role played by solvent in the polymer film molecular orientation.

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and surface energy. Figure 2 shows SFG spectra obtained in air for CAP adsorbed from acetone (Figure 2a) and ethyl acetate (Figure 2b). Although the intensities in the latter are stronger than in the former, both spectra presented one band at ~2882 cm\(^{-1}\) and another one at 2950 cm\(^{-1}\), which were assigned to the CH\(_3\) symmetric stretch (CH\(_3\) (s)) and to the Fermi resonance between the symmetric-stretch fundamental and an overtone of a bending mode of CH\(_3\) (CH\(_3\) (F)), respectively. Such characteristics bands were also observed for other polymeric interfaces [34-38] and systems formed by small molecules [39-43], where methyl groups are oriented perpendicularly to the surface. The larger intensities observed for CAP adsorbed from ethyl acetate solutions (Figure 2b) than those for CAP films formed from acetone solution (Figure 2a) indicated that in average a larger number of methyl groups were oriented perpendicularly to the surface when ethyl acetate was used as solvent. Such preferential orientation corroborates with macroscopic contact angle measurements, which showed that CAP films are more hydrophobic when adsorbing from ethyl acetate (Table 1).

SFG spectra obtained in air for CAB adsorbed from acetone and ethyl acetate (not shown) presented weak intensity bands with the following assignments: 2878 cm\(^{-1}\) CH\(_3\) (s) and 2945 cm\(^{-1}\) CH\(_3\) (F). CAB films prepared from ethyl acetate showed two intensive bands at 2879 cm\(^{-1}\) and 2942 cm\(^{-1}\), which were assigned to CH\(_3\) (s) and CH\(_3\) (F), respectively. Similarly to CAP films, the spectra obtained for CAB indicated that ethyl acetate induces more efficiently the orientation of methyl groups perpendicularly to the surface than acetone, explaining the more hydrophobic nature of CAB films adsorbed from ethyl acetate (Table 1). Interestingly, spectra obtained for CAP and CAB showed no bands in the carbonyl typical spectral range from 1600 cm\(^{-1}\) to 1800 cm\(^{-1}\) (not shown), indicating random orientation of carbonyl groups or absence of carbonyl group oriented perpendicularly to the surface.

In a three component system, where solvent and polymer might compete for the substrate, the characteristics of resulting adsorbed layer depends on the affinity between polymer and solvent, polymer and substrate and solvent and substrate. In order to gain insight about the affinity between solvent and substrate SFG spectra were obtained for acetone and ethyl acetate onto quartz slides (Spectra not shown). In the case of acetone, an intense band at ~ 2923 cm\(^{-1}\) was assigned to the symmetric stretch vibration mode of methyl group of acetone (CH\(_3\) (acetone)) [43]. In the case of ethyl acetate the intensities were too weak to make any assignment. These findings indicate strong affinity between acetone and SiO\(_2\) surface and weak affinity between ethyl acetate and SiO\(_2\) surface and corroborate with literature reports [24]. The strong adsorption of acetone onto SiO\(_2\) creates in situ a new layer between CAP or CAB and SiO\(_2\), which stabilizes the thin polymeric film avoiding dewetting phenomena. On the other hand, the adsorption of ethyl acetate onto SiO\(_2\) seems to be
weak, and polymer layers face SiO$_2$ directly. In that case, film stability is controlled by polymer/polymer attraction ($A_{\text{poly/poly}}$) and polymer/substrate interaction ($A_{\text{poly/substrate}}$).

**Figure 2** – SFG spectra obtained in air for dried CAP films adsorbed from (a) acetone and (b) ethyl acetate solutions.

SFG spectra obtained *in situ* for acetone onto SiO$_2$ (not shown) evidenced preferential orientation of methyl groups perpendicular to the surface. After *in situ* measurements, SiO$_2$ slides were dried under a stream of N$_2$ and new SFG spectra were recorded. A band at $\sim$2955 cm$^{-1}$, assigned to methyl groups, became weaker, indicating that even after drying acetone can not be totally removed from SiO$_2$ surface. Another indication that methyl groups are predominantly oriented perpendicularly to the surface was confirmed by contact angle measurements with water drops, which amounted to $(40 \pm 2)^{\circ}$. For comparison contact angle for water onto clean SiO$_2$ is typically $5^{\circ}$ [18]. Therefore, these findings prove that acetone molecules bind strongly to SiO$_2$ surfaces.

**Conclusions**

Many technological processes apply polymer solutions for the production of polymer films. The present work has shown that the solvent used for polymer films formation might play a crucial role on interface properties and polymer film stability. Acetone binds strongly to SiO$_2$ surfaces due to acid-base interactions, creating a new surface for CAP or CAB, which avoids dewetting. The ability of this new surface to induce alkyl groups’ orientation to the polymer-air interface is limited, leading to more hydrophilic surfaces. Ethyl acetate was able to induce perpendicular orientation of CAP or CAB alkyl groups to the polymer-air interface. This preferential orientation led to
hydrophobic surfaces, but film stability was driven by polymer surface energy and interface tension between substrate and polymeric film. From the experimental point of view, SFG proved to be an excellent complement for AFM and contact angle measurements, providing information at molecular level and giving support for macroscopic data.

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References