

Structure and interfacial interactions of thin films of amylopectin

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Structure and interfacial properties of micrometer-thick amylopectin films were investigated. The polysaccharide amylopectin forms the crystalline regions in native starch. By applying X-ray scattering at wide and small angle detection modes, and surface microscopy (phase interference microscopy and atomic force microscopy), we were able to probe the film structure and the surface morphology. The thin films were found to be amorphous with some degree of orientational order in the direction normal to the surface. A step-like surface morphology was observed, with a typical step-height of 100 nm and lateral dimensions of 100 μm . We investigated the interfacial interaction between amylopectin and polystyrene and found that the stability of polystyrene films on top of the amylopectin substrate depends on film thickness: thin films (adsorbed layers of a few nanometers) were stable due to short-range interactions, while thicker films (of a few hundred nanometers) dewetted due to van der Waals interactions.

1. Introduction

Thin films of synthetic polymers have been studied extensively from both applied and fundamental points of view. In a thin film configuration, interfacial interactions are expected to modify bulk properties, as indeed was found experimentally for optical properties [1], the glass transition temperature [2–4], viscosity and diffusivity [5]. Much less experimental work has been carried out for the characterization of sub-micrometer films of natural polymers. These systems are more complex due to the many relevant parameters and interactions of their constituents. For example, starch, which is the most abundant natural polysaccharide [6], consists of two high-molecular-weight components: amylose and amylopectin. Both polymers are highly polydisperse, display different degrees of branching, and a high degree of hydrogen bonding. While the amylose molecules are linear and form an amorphous

solid, the amylopectin molecules are highly branched and crystalline. The branching points in the amylopectin molecule are clustered and form lamellar domains with a typical repeating distance of 5–7 nm [7]. Each cluster contains about 9–17 side chains, which are coiled into double helices. The different modes of organization and the relevant length scales are shown schematically in Fig. 1.

The multi-level structuring of amylopectin and other natural polymers determines their physical properties in the bulk. When these materials are confined into films thinner than a few micrometers, their structural hierarchy is disturbed by the very confinement, and additionally altered by the action of surface forces. Thus, it is expected that the bulk structure and the resulting physical properties will be modified in a thin film. Additionally, the surface may exhibit a non-random morphology unlike the smooth and structureless texture of synthetic amorphous polymers.

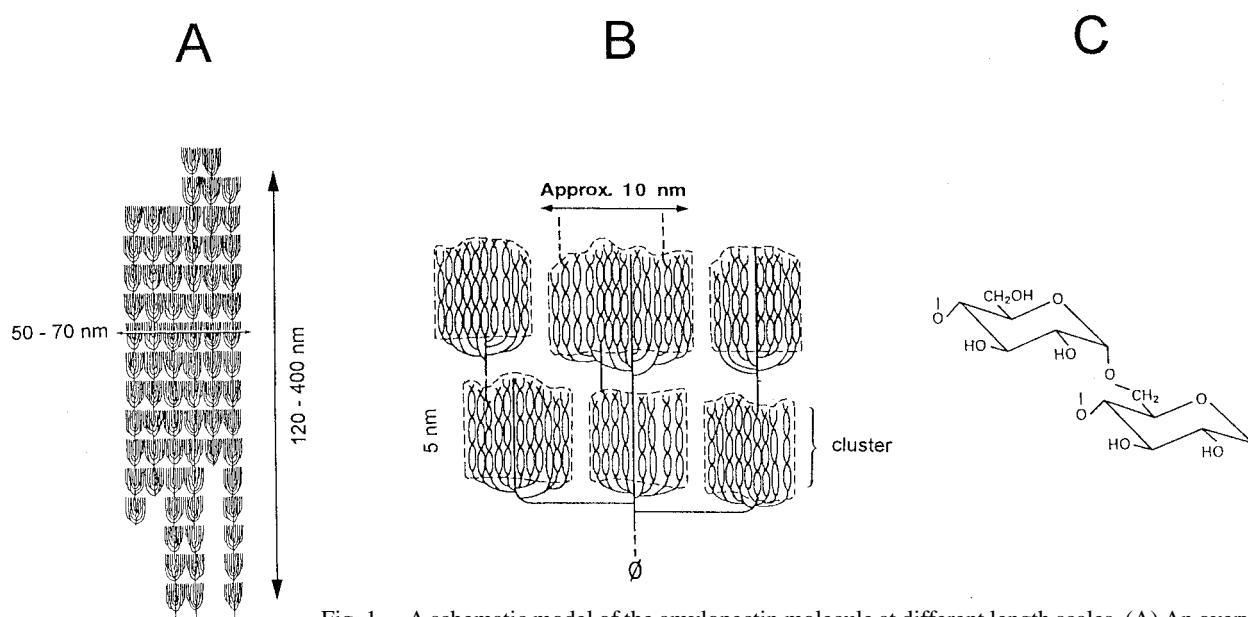


Fig. 1. A schematic model of the amylopectin molecule at different length scales. (A) An overview of the amylopectin molecule, presenting the clustering of the branching points. The long axis of the molecule is of some hundreds of nanometers. (B) A close view of the double helical conformation of adjacent linear chains forming 5–7 nm lamellae. (C) Molecular structure of the D-glucose monomers forming the linear chains. (Adapted from J.P. Robin et al., *Cereal Chem.* **1974**, *51*, 389, D.J. Gallant et al., *Carbohydr. Polym.* **1997**, *32*, 177, and [6].)

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The surface morphology of thin films is an important feature of the system, as it affects strongly interfacial interactions such as wetting, adsorption and adhesion [8–10]. Here we describe an experimental investigation of the structural properties of amylopectin films in the thickness range of a few micrometers, by small and wide angle X-ray scattering (SAXS and WAXS, respectively), surface topography by atomic force microscopy (AFM) and optical phase modulated interference microscopy (OPIM). Adsorption and wetting behavior of thin films of polystyrene on top of the amylopectin substrate were studied by nuclear reaction analysis (NRA) and optical microscopy.

2. Experimental

2.1. Materials

Amylopectin was purchased from Sigma (A-7780 from Corn) and used as received. Amylopectin is a (1→4)- α -D-glucan, highly branched through (1→6)- α -linkages and polydisperse. The average degree of polymerization varies between 1 and 50 million [6]. Amylopectin is insoluble in cold water but may be dissolved in hot water ($T > 50^\circ\text{C}$).

Polystyrene, either protonated or fully deuterated, was purchased from Polymer Laboratories. The characteristics of the polymers were determined by size-exclusion chromatography and provided by the suppliers. Polymer characteristics are given in Table 1.

The toluene used was Frutarom or Sigma analytical grade. Water was purified by a Barnsted E-pure water purifier (measured resistivity of 18 M Ω).

Polished silicon wafers (p-type, <100>, 0.5–1 $\Omega\text{ cm}^{-1}$, thickness of 406–470 μm) were purchased from ITME (Warsaw, Poland).

2.2. Sample preparation

2.2.1. Thin films of amylopectin

Amylopectin solutions in water (30 mg/ml) were prepared by heating solid amylopectin in water to above 70°C for about 10 min, until the solution changed from milky to opalescent. The viscous warm solution was then spin-

coated on top of silicon wafers and the films were dried at ambient conditions. By spin-casting at different rates, films of different thickness (in the range of a few micrometers) could be prepared.

2.2.2. Adsorption of polystyrene

Adsorption experiments were performed by incubation of amylopectin-coated silicon wafers in dilute toluene solutions of polystyrene (0.1 mg/ml) for 12–15 h, followed by thorough wash in pure toluene, to remove the non-adsorbed polymer, and drying in ambient conditions for a few days. Toluene is a good solvent for the polymer but does not dissolve amylopectin.

2.2.3. Wetting experiments – amylopectin–polystyrene bilayers

Films of polystyrene in the thickness range of 50–400 nm were prepared on top of amylopectin substrates. As toluene is a selective solvent, bilayers could be prepared by directly coating polystyrene on top of the amylopectin films. The thickness of the polystyrene layers was controlled by the spinning frequency and the concentration of the solutions, and measured by NRA as described below.

The amylopectin–polystyrene bilayers were annealed for different time intervals and temperatures. For annealing at temperatures $T > 60^\circ\text{C}$ the samples were sealed in glass ampoules under vacuum (5×10^{-3} Pa). After annealing, the samples were rapidly quenched to a temperature below the glass transition temperature of polystyrene.

2.3. Characterization of the system

2.3.1. Small and wide angle X-ray scattering (SAXS and WAXS)

The X-ray measurements were performed on a Kratky compact system equipped with two position-sensitive detectors (OED 50M from MBraun, Graz, Austria), each containing 1024 channels of 51.4 μm width for simultaneous small and wide angle measurements (SWAX). Our detection range for small and wide angle measurements was, respectively, $0.5^\circ < 2\theta < 8^\circ$ and $17^\circ < 2\theta < 23^\circ$. Cu- K_α radiation of wavelength $\lambda = 0.1524$ nm was provided by a Seifert ID-3000 X-ray source, operating at 40 kV and 40 mA. A 10 μm thick nickel filter was used to remove the K_β radiation, and a 1.5 mm tungsten filter was used to protect the detector from the main beam. The sample-to-detector distance was 277 mm. In the structural analysis the peak positions of SAXS spectra were determined at the q -values, $q = 4\pi\sin(\theta)/\lambda$, giving the maximum intensity. Full spectra ($3^\circ < 2\theta < 30^\circ$) of powders were obtained from a Philips generator operated at 40 kV and 28 mA equipped with a graphite monochromator, PW1050-70 goniometer and a scintillator detector. Since the morphological features are much smaller than the particle size, and the overall orientation is uniform, SAXS spectra of powder were analyzed using the Guinier approximation [11] assuming a

Table 1. Molecular characteristics of oligostyrene and polystyrenes.

Material	Weight averaged molecular weight M_w [g/mol]	Designation	Polydispersity M_w/M_n
Oligostyrene	580 ^a	PS-0.58k	1.02
Polystyrene	330000	PS-330k	1.04
	526000	PS-526k	1.04
Deuterated polystyrene	10500	dPS-10.5k	1.02
	370000	dPS-370k	1.02

^a The glass transition temperature of PS-0.58k is $T_g = -18^\circ\text{C}$. For the other polystyrene samples $T_g = 100^\circ\text{C}$.

non-interacting and globular pattern. All samples were measured in sealed glass capillaries. The thin-film samples were prepared by scratching a thin film (of few micrometers thickness) off of the silicon wafer (diameter of 7.5 cm) on which it was prepared, and filling a capillary with the powder.

2.3.2. Optical phase interference microscopy (OPIM)

The surface morphology of thin amylopectin films was investigated by OPIM. This is an interference technique in which the interference pattern is recorded by a (charge-coupled device) (CCD) camera, and processed by computerized image analysis, mapping the data carried by interference fringes into a detailed, three-dimensional image. The measurements were performed on a Zygo Maxim-3D system at the Max-Planck-Institut für Polymerforschung (Mainz, Germany). This technique combines sub-nanometer resolution in the vertical direction with micrometer-range spatial resolution and a large field of view ($418 \times 418 \mu\text{m}^2$) [12].

2.3.3. Atomic force microscopy (AFM)

Surface roughness and structure at a nanometric scale were studied by AFM, using a Topometrix TMX2010 Discoverer system with etched silicon tips on a cantilever (Nanosensor) of spring constant k ranging between 0.1 and 0.3 N/m and a tip size of 15 nm (as specified by the manufacturer).

2.3.4. Nuclear reaction analysis (NRA)

We used NRA to determine the thickness of the polystyrene layers, on top of amylopectin substrates, in the bilayer

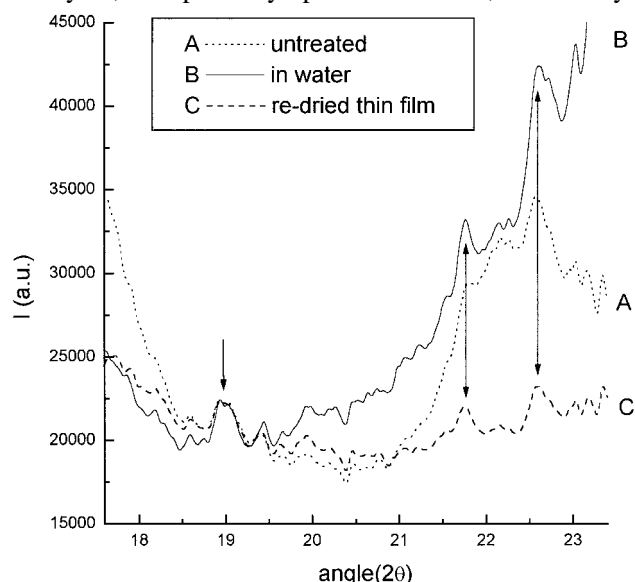


Fig. 2. WAXS measurements of amylopectin (A) untreated, (B) dissolved in water, and (C) dried as a thin film. The small shoulders (see the arrows) in the $2\theta > 21^\circ$ region, are preserved throughout the treatment. These shoulders are assigned to the double helical conformation of the amylopectin side chains. Comparison of the spectra of the untreated amylopectin (A) with (B) and (C) suggests that the crystalline structure is lost.

configuration. In this method [13, 14] a monoenergetic ^3He beam is incident at low angle on a sample that contains deuterated species undergoing the nuclear reaction $^3\text{He} + ^2\text{H} \rightarrow ^4\text{He} + ^1\text{H} + Q$ ($Q = 18.35 \text{ MeV}$). The measured energy spectrum of the reaction products provides directly the film thickness. The use of NRA for thickness measurements was required because standard methods [15] such as ellipsometry and X-ray reflectivity are not applicable on the textured amylopectin–thin film interface as the measurement is disturbed by surface roughness and structuring. NRA measures the energy loss of a particle traveling through the layer of deuterated material and allows us to determine the film thickness with an uncertainty of about 10%, in the thickness range of 100–800 nm (but > 50% for thinner films). The uncertainty in the thickness results from a reduced resolution due to the step-like topography of the amylopectin surface [16]. The NRA measurements were performed at the Van de Graaff accelerator of the Weizmann Institute, Rehovot, Israel.

3. Results

3.1. Structural characterization of amylopectin

The structure of amylopectin films was investigated by X-ray scattering using both the wide angle (WAXS) and small angle (SAXS) modes of detection. Preparation of the thin films involves dissolution of solid amylopectin in water, and re-drying. This treatment is known to affect the structure of amylopectin, and in particular the type and degree of crystallinity of the re-dried material [6]. We therefore investigated thoroughly the structure of untreated amylopectin, amylopectin in aqueous solutions, re-dried amylopectin in the bulk, and thin films of amylopectin. In the following we describe the results of WAXS and SAXS experiments.

3.1.1. WAXS measurements

The WAXS pattern of the untreated amylopectin consists of two sets of peaks, distinguished by their location and intensity. The first set of high intensity peaks is located at the region of $2\theta < 26^\circ$, and corresponds to the typical A-type pattern of amylopectin [6]. We measured the complete spectrum and found our results consistent with the literature [6]. Two peaks of this spectrum (at 17° and 22°) are shown in Fig. 2A as obtained by our WAXS detector (limited to $17^\circ < 2\theta < 23^\circ$). The A-type structure is known to result from the nearly close-packed arrangement of amylopectin double helices. This set of peaks disappears almost completely in the aqueous solution, and does not reappear on drying (B and C of Fig. 2). The second set of small-but-sharp peaks in the region of $19^\circ < 2\theta < 23^\circ$ appears in the untreated powder, in the solution as well as in the dried powder (note arrows in Fig. 2B, C). These peaks are assigned to the double helices formed by the linear segments of the amylopectin molecules [17]. To further test this interpretation, we measured the WAXS spectra of amylopectin in glycerol. Glycerol is known to form com-

plexes with amylopectin, and thus is expected to disrupt completely the characteristic double-helix conformation [18]. Indeed, the WAXS spectra of amylopectin solutions in glycerol (not shown) do not show the second set of peaks like those of Fig. 2.

3.1.2. SAXS measurements

The small-angle range of X-ray scattering is sensitive to the presence of structures with a typical length scale in the range of 1–60 nm. In Fig. 3 we compare the spectra of the untreated amylopectin powder with that of treated amylopectin re-dried in the bulk and the thin-film configuration. In the untreated powder we detect the presence of characteristic lengths that correspond to spacings of 7.5 nm, and 4 nm. The first may be attributed to the lamellar structure of the side-chain clusters of the amylopectin molecule. The broad and low-intensity shoulders indicate that the degree of ordering is low. Using the Guinier approximation [11] for the untreated powder and the thin film, assuming a globular shape of some scattering particles, we estimate that their typical radius of gyration is in the range of 3 nm.

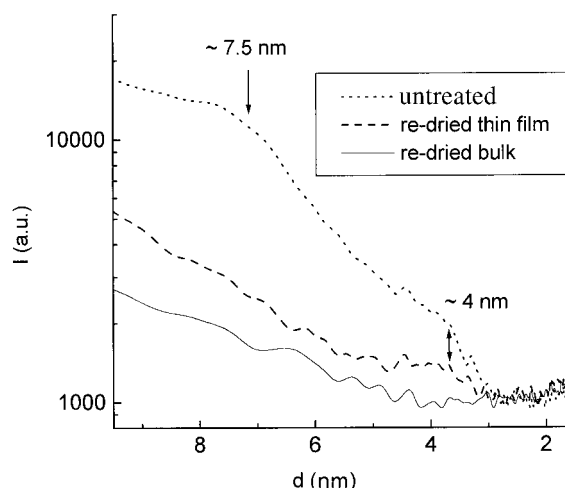


Fig. 3. SAXS measurements of amylopectin untreated (dotted line), re-dried in the bulk (dashed line), and re-dried as a thin film (solid line). The scattering pattern is presented as intensity vs. lattice spacing d . The spectrum of the untreated material contains shoulders at 7.5 nm and 4 nm. While the first peak does not appear in the treated material, the 4 nm peak is preserved in the thin film.

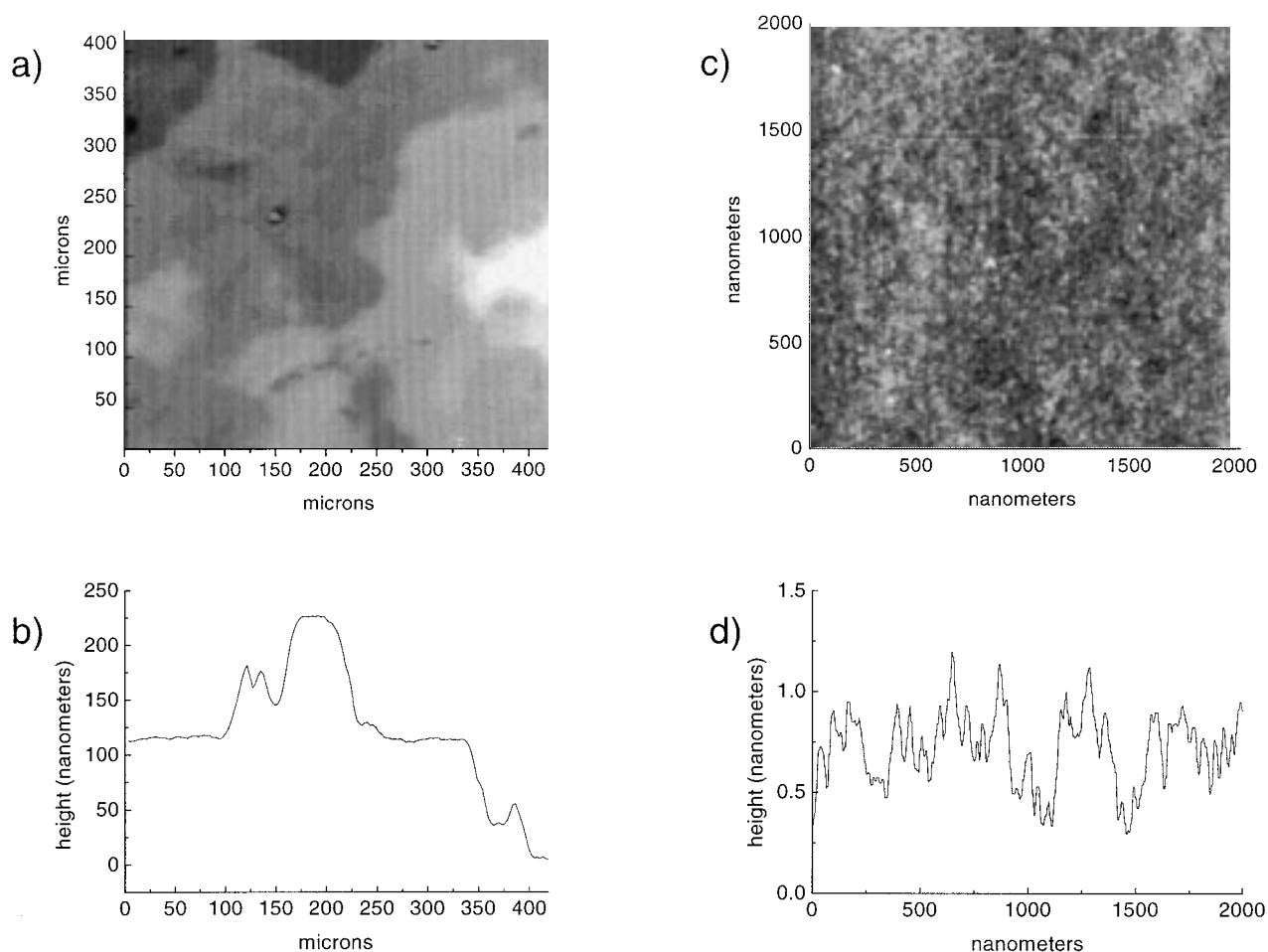


Fig. 4. An amylopectin film on top of a silicon wafer. The film was scanned by OPIM (a, b) and AFM (c, d). (a) An OPIM image of the surface, the lateral dimensions are $418 \times 418 \mu\text{m}^2$, the vertical scale is 250 nm. The different gray-scale levels correspond to the height distribution of the sample surface. The baseline of the presented image was corrected (by subtraction of a second-order polynomial). (b) A line scan through the image, presenting the relative heights along the sample. (c) An AFM image of the surface, presenting an overview of the surface at a higher magnification with lateral dimensions of $2 \times 2 \mu\text{m}^2$, and a vertical scale of 2 nm. (d) A line scan through the image presenting random roughness in the range of 2 nm.

The SAXS spectra of the re-dried amylopectin films retains the structure at 4 nm, while the spectrum of the amylopectin re-dried in the bulk does not show any special structure.

3.1.3. Birefringence measurements

Thin films of re-dried amylopectin viewed between crossed polarizers show birefringence while the aqueous solutions and the bulk-dried amylopectin are optically isotropic.

3.2. Surface characterization of amylopectin films

OPIM and AFM were used to characterize the surface topography of amylopectin films. The two methods differ in the lateral resolution (micrometers for OPIM, nanometers for AFM) and in the field of view (as described in the experimental section). The combination of the two methods enables us to observe the characteristic surface morphology at length scales ranging from nanometers to some hundreds of micrometers, with height sensitivity in the range of nanometers. In Fig. 4 we present two images of the surface, measured by OPIM (Fig. 4a, b), and by AFM (Fig. 4c, d). The line scan through the OPIM image (Fig. 4b) presents a typical step pattern of the surface. The characteristic step-height is about 100 nm and the lateral dimension of a step is in the range of 100 μm . The AFM image and the line scan through it (Fig. 4d) present a relatively smooth surface, with random root-mean-squared (rms) roughness < 2 nm. As the lateral dimensions of the steps are far larger than the field-of-view of the AFM scan, they are not observed in that scan. In Fig. 5 we analyze the OPIM data. We observe (Fig. 5a) that the height distribution of the surface steps is rather narrow around the typical value of 100 nm and reproducible in different samples (Fig. 5b).

Our results suggest that the surface topography of amylopectin films depends on the length scale of observation, presenting a topography of wide steps (typical area of 100 μm^2) and a narrow height distribution (around 100 nm).

3.3. Adsorption experiments

We studied the adsorption of deuterated polystyrene dPS-10k and dPS-380k from toluene solutions on amylopectin substrates. The samples were incubated in the solution, thoroughly washed in the solvent, dried, and measured by NRA. In Fig. 6 we present an NRA spectra which reveals the presence of a thin dPS layer on top of the amylopectin surface. As the thickness of the adsorbed film is in the range of the resolution limit of the technique for the structured amylopectin surface, we only use the NRA data as a qualitative indication for the presence of an adsorbed layer [19]. We find that polystyrene adsorbs spontaneously from toluene solutions on top of the amylopectin surface.

3.4. Wetting experiments

The wetting behavior of deuterated and protonated polystyrenes on the amylopectin substrate was investigated for different molecular weights (PS-0.58k, dPS-10.5k, PS-330k, dPS-370k, PS-500k). Films of polystyrene in the thickness range of 50–400 nm were spin-coated on top of amylopectin substrates and annealed above the glass transition temperature of the polymers. The liquid films were found to be unstable, and dewetted into droplets. We compared the pattern formed by the liquid droplets of polystyrene dewetting on amylopectin substrate to that formed on a silicon wafer. For that purpose, we prepared silicon wafers half-covered by amylopectin. A (deuterated) polystyrene film was then spin-coated on top of the whole wafer and annealed. In Fig. 7 we present a picture of a dewetted film. NRA was used to measure the thickness of the deuterated polystyrene layer (before annealing) on both parts of the wafer in similarly prepared samples. The NRA profile is presented in Fig. 8. We observe that the initial thickness of the polystyrene film is similar (Fig. 8 (\circ) and (\blacksquare)), however, the droplet pattern formed by the dewetted layer is remarkably different (Fig. 7 A and B). The polygonal pattern observed on the silicon side, with droplets forming a smooth contact line at the solid–liquid interface, is typical for polystyrene films dewetting on a smooth silicon wafer

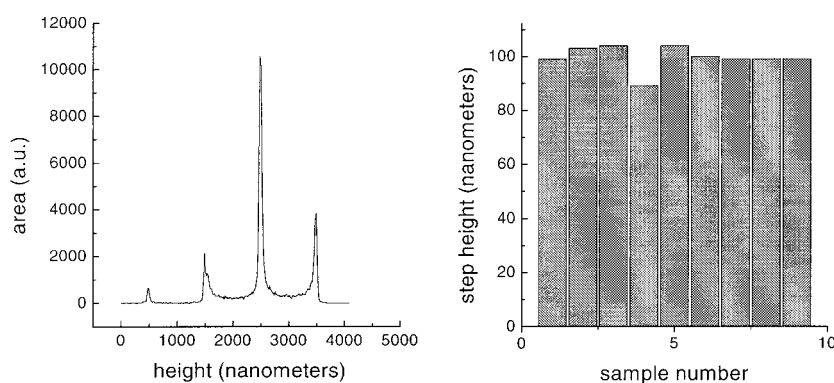


Fig. 5. Analysis of OPIM images of thin films of amylopectin. (a) A histogram presenting the distribution of relative heights at the amylopectin surface. (b) Data collected from images of different samples.

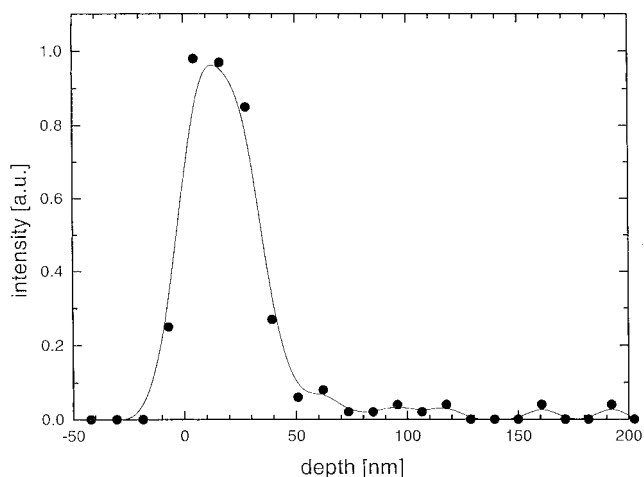


Fig. 6. NRA profile of an adsorbed layer of dPS-380k on top of an amylopectin substrate. The sample was prepared by incubating the substrate in a toluene solution (0.1 mg/ml) of dPS-380k followed by thorough washing in the solvent. The sample was then dried in ambient conditions for a few days and measured by NRA. The spectrum indicates the presence of a thin layer at the amylopectin surface (at zero depth in the graph).

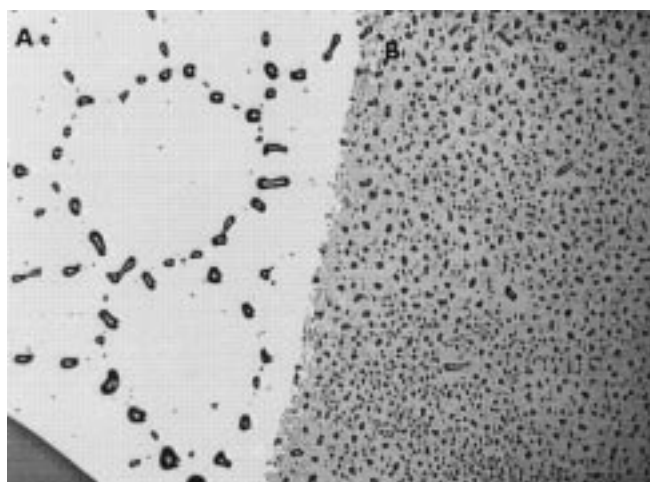


Fig. 7. An image of a dPS-10.5k film following a week of annealing at 160 °C, under vacuum (5×10^{-3} Pa). In this sample the polystyrene film was coated on top of a silicon wafer half covered by a thin film of amylopectin (forming a bilayer) (A) and on top of the silicon surface (B). The droplets result from dewetting of the initially homogeneous polystyrene film. The image displays an area of 1×0.75 cm².

[20]. On the other hand, the droplet pattern on the amylopectin surface seems to be random, with droplets of distorted shape and form.

The instability of polystyrene films on the amylopectin surface may seem to be inconsistent with the results of the previous section, which indicate that the polystyrene adsorbs spontaneously on the amylopectin substrate. To further investigate that point, we performed the following experiment: a layer of dPS-380k was pre-adsorbed on amylopectin substrate (according to the procedure described before). Then, a thin film of oligostyrene (PS-0.58k, thickness of 100 nm and 300 nm, liquid at room

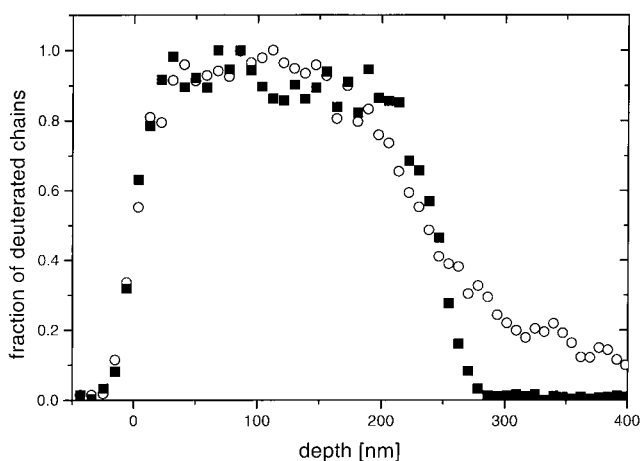


Fig. 8. NRA profiles measuring the volume fraction versus depth of a thin film of dPS-10.5k, spin-coated on top of a silicon wafer (n), half of which was covered by amylopectin (o). Zero depth is the dPS-air interface, and the cutoff at about 250 nm is the film-silicon interface. The resolution at the amylopectin-dPS interface (■) is much worse than the resolution at the silicon-dPS interface, as discussed in the text. Within the limits of the resolution, the thickness of the film on both parts of the substrate is similar.

temperature) was formed on top of the adsorbed layer by spin-coating from solution. We observed that the film was unstable and dewetted into a similar random pattern of droplets as the one presented in Fig. 7. These observations indicate that the presence of a thin adsorbed layer does not stabilize thicker films of polystyrene on top of amylopectin. We conclude that polystyrene adsorbs spontaneously from solution on amylopectin, while thicker films (thickness of 50–400 nm) are unstable and dewet even in the presence of a pre-adsorbed layer.

4. Discussion

In this study we investigated the bulk structure, surface morphology, and wetting properties of micrometer-thick amylopectin films. We discuss first the structure of the films and the surface morphology.

The structural features of amylopectin at length scales below 100 nm were probed by WAXS and SAXS. The results indicate a loss of long-range crystalline order upon dissolution, which is not restored by drying. However, the SAXS spectra also reveal that a structure with a typical repeat distance of 4–5 nm present in the untreated amylopectin is preserved in the re-dried material. We suggest that the origin of that typical ordering is in the intra-molecular double-helix conformation of the amylopectin molecule. Our results then indicate that the double-helix conformation of the side chains is not completely lost in the process [21]. The observed birefringence of amylopectin thin films, together with the optical isotropy of amylopectin that was treated similarly but dried in the bulk, suggests that the packing of amylopectin molecules in a thin film induces some degree of orientational order [22]. The effect

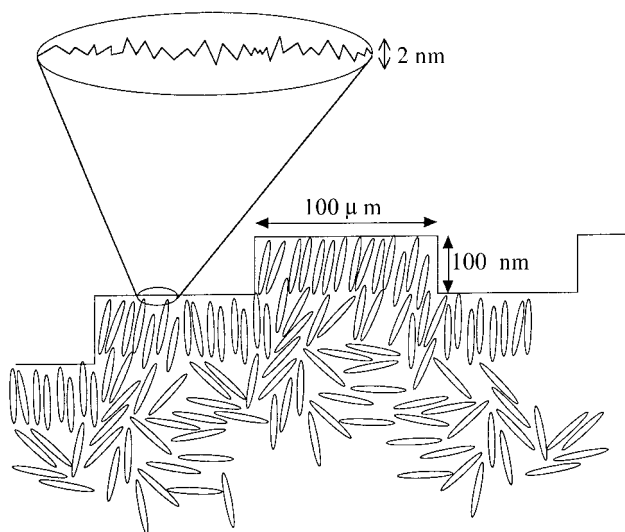


Fig. 9. A schematic illustration of amylopectin molecules packed in a thin film. The axial ratio of the molecules and the degree of orientational order near the surface are exaggerated. A magnified picture of the surface presents the low-scale roughness.

may be related to the geometrical anisotropy of the molecules, which are elongated with a long axis of about 120–400 nm (depending on the botanical source) and a short axis of about 50–70 nm (Fig. 1a). In the thin film, surface interactions act as a non-random force that orients the molecules. As the repeat distance in the film is in the range of 100 nm, it is not detected by the X-ray scattering in either the WAXS or the SAXS modes.

The surface morphology of the amylopectin films, as detected by OPIM and AFM, reveal a step-like topography of narrow step-height distribution around 100 nm, and lateral step dimensions in the range of 100 μm. A low level of random surface roughness (rms value of about 2 nm) is detected by the AFM. The observed surface texture is consistent with the notion of amylopectin molecules displaying a preferred orientation of the long axis of the molecule in the direction normal to the surface, rather than packing at random. We present the information concerning the film structure and surface topography in a schematic drawing (Fig. 9).

The results of the adsorption and wetting experiments at the polystyrene–amylopectin interface reveal that the stability of a polystyrene film on top of the amylopectin substrate depends on the thickness of the layer: while a monolayer of polystyrene adsorbs spontaneously from solution, thicker layers of polystyrene that are forced to spread on the amylopectin surface dewet. Moreover, thin films of the oligomeric PS-0.58k are unstable on top of a pre-adsorbed layer of polystyrene and dewet as well.

We discuss the wetting behavior in terms of models derived for describing the interfacial interactions of non-volatile liquid films with solid surfaces [23–25]. The free energy per unit area, f , of a film of thickness h is described by:

$$f = -S + V(h) \quad (1)$$

S is the spreading coefficient that describes the short-range interactions and accounts for the change in the free energy due to spreading or adsorption [25]

$$S = f_{\text{dry}} - f_{\text{wet}} = \gamma_{\text{sv}} - (\gamma_{\text{sl}} + \gamma_{\text{lv}}) \quad (2)$$

where s, l, and v stand for solid, liquid and vapor and γ_{ij} is the surface tension between the i and j phases. Thus, spreading is favored when $S > 0$. The term $V(h)$ describes the long-range interactions. In the case of a van der Waals liquid

$$V(h) = A/12\pi h^2 \quad (3)$$

where A is the effective Hamaker constant for the interaction of the solid and air media across the liquid medium [27]. At equilibrium, the van der Waals interactions tend to thin the liquid film when $A < 0$ and thicken it when $A > 0$.

In Table 2 we summarize the relevant parameters for a polystyrene film and an amylopectin surface.

From the values of the surface tension we estimate [32] that the spreading coefficient is positive, and from the relations between the refractive indices [27] we find that the effective Hamaker constant is negative. The combination of $S > 0$ and $A < 0$ designates this as a case where a thin film of the liquid is stabilized by the short-range interactions, but a thicker film becomes unstable due to van der Waals interactions. In this case, a film thicker than the range of the short-range interaction (≈ 10 nm [33]) is expected to be unstable and equilibrate by dewetting into macroscopic droplets in contact with a thin liquid film. In the notion of the Brochard model [25] this is designated as “pseudopartial wetting”. The predicted strong dependence of film stability on film thickness agrees well with the experimental observations. In particular, it is consistent with the observation that while an adsorbed monolayer of polystyrene is stable on the surface of amylopectin, a thicker film of polystyrene is unstable and dewets.

The last point in our discussion relates to the random distribution of polystyrene droplets on top of the amylopectin substrate and their shape. Polystyrene films of uniform thickness that dewet on top of a smooth surface are known to form a polygonal-like droplet pattern, similar to that observed in Fig. 7A. The polygonal pattern results from the simultaneous expansion of randomly distributed circular holes, which grow until they coalesce [9, 34]. We believe that the step-like morphology of the amylopectin surface disrupts the dewetting process by pinning the con-

Table 2. Parameters for the description of wetting behavior.

Material	Refractive index	Surface tension [mJ/m ²]
Polystyrene	1.571–1.591 [28]	33–38 [29]
Amylopectin	$n_0 = 1.523$ $n_e = 1.535^a$ [30]	

^a At 589 nm; n_0 is the ordinary refractive index and n_e the extraordinary refractive index.

tact line of the receding liquid. Thus, droplets form (due to Rayleigh instability [20]) before holes coalesce, and the polygonal pattern is not observed. The effect of pinning also contributes to the non-relaxed droplet shape.

5. Conclusions

We demonstrated that it is possible to characterize the structure and surface morphology of thin films of a complex material such as amylopectin by a combination of experimental techniques that are sensitive to structures at different length scales. We found that amylopectin molecules that are confined in a thin film show surface-induced orientation and a step-like surface texture. The interfacial interactions between thin polystyrene films and the amylopectin films was found to depend strongly on the thickness of the polystyrene film, suggesting that, in this system, the interplay between short-range polar interactions and long-range van der Waals interactions leads to thickness-dependent stability.

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$$A = \frac{3}{4} kT \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_3} \right) \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right) + \frac{3h\nu_e}{8\sqrt{2}} \times \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{\sqrt{n_1^2 + n_3^2} \sqrt{n_2^2 + n_3^2} (\sqrt{n_1^2 + n_3^2} + \sqrt{n_2^2 + n_3^2})}$$

with ϵ_i and n_i the static dielectric constant and the optical refractive index of medium i , respectively, ν_e the electronic absorption frequency, which is assumed to be equal for all three components.

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