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Smart Surfaces of Biobased Materials. III. Surface segregation in Cellulose Ester Films

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Abstract:

The surface of solvent cast films of blends of cellulose propionate and fluorine (F)-containing cellulose derivatives was examined. Static wetting force measurements of blends showed a sharp decline in wetting force at low blend concentrations of the F-species. This indicated enrichment of the F-containing derivative at the surface. X-ray photoelectron spectroscopy (XPS) of blends revealed a surface concentration of F higher than by blend composition, verifying surface segregation. The extent of surface segregation was a function of the nature of the F-component and its blend concentration. Angle dependent XPS measurements revealed an F-gradient with sampling depth with the highest F-content found in the top 30 nm-layer. Limited surface heterogeneity, depending on the type of F-derivative was detected by phase-image atomic force microscopy.

Introduction:

The surface properties of polymers play an important role in such fields as wetting and adhesion[1], composites[2], lubrication and friction[3]. It is commonly known that the surface composition of a polymer blend is usually different from that of the bulk. The preferential adsorption of one moiety at the surface is known as surface segregation[4]. The process is a thermodynamically driven process and has been subject of numerous theoretical treatments[5,6]. Thermodynamics dictate any system to adopt the state of lowest free energy and as a consequence the component with the lowest surface free energy is segregated to the surface. Surface segregation is therefore a convenient method to create materials with surfaces that are more hydrophobic than the bulk phase.

The process of surface segregation can be triggered by either energetic or enthalpic factors. Enthalpic factors include differences in molecular weight[7,8] and chain stiffness[9], including differences in surface free energy[10]. Differences in surface free energy are due to the presence of atoms other than hydrogen in hydrocarbons. Already minor energetic differences like differences between deuterated and hydrogenated species results in surface segregation[11]. Fluorine-containing molecules are known for their low surface free energy, which is caused by the low polarizability of the C-F bond. Strong surface segregation has been observed in a number of F-containing polymer blends[12-15]. Since a blend has a limited reservoir of the segregation species, surface segregation almost always results in the bulk depletion of that species[16].

X-ray photoelectron spectroscopy is a well-established tool for the determination of the atomic composition of the surface and as such has found wide use in the investigation of surface segregation. The possibility to conduct measurements at different sampling depth allows following the declining concentration of the segregating species into the bulk of the material.

Previous papers in this series[17,18] have reported on the behavior of fluorine (F)-containing derivatives of cellulose esters. Two types of behaviors were described for esters being structurally distinct. Surface segregation of F-containing cellulose esters was indicated when the cellulose ester molecules had F-containing substituents distributed randomly along their backbone; and the formation of micelles by self assembly was observed when the F-substituents were attached to cellulose ester oligomers as monofunctional termini at one end of the molecule. The synthesis of these various F-containing cellulose ester derivatives has been the subject of prior publications.

This paper is to examine aspects of the surface segregation of F-containing random cellulose ester derivatives in relation to specific structural configurations.

Experimental:

Materials:

Cellulose propionate was purchased from Aldrich Chemical Company. Tetrahydrofuran was from Fisher Scientific and used as received. Statistical F-esters, i.e. cellulose ester derivatives with F-containing ester groups evenly distributed along the backbone, were synthesized in our laboratory as described elsewhere[19,20].

Methods:

Blend Preparation: Cellulose propionate (CP)/ terminated segment (CP-F) blends were prepared by mixing the appropriate volumes of stock solutions (5% w/v) to the desired content of F-containing species, keeping the total solids content of all solutions at 5% w/v. The concentration of F-species in a blend is given as the mass % value of F-species with respect to the total amount of solids.

Wetting force Measurements: Wetting force measurements were based on a modified Wilhelmy Plate method. Microscope cover slides were cleaned thoroughly in hexanes, wiped dry with lint-free Kimwipes, and subsequently dip-coated (one coat) with the respective solutions. The glass slide served as a sinker to ensure that the films would submerge in the wetting liquid. The solvent was evaporated at 4°C (refrigerator) over night and all films were stored polypropylene containers for three days before the wetting force measurements were carried out. Care was taken to ensure that all films were prepared in the same fashion. The wetting force measurements were conducted with deionized water as the wetting medium using a CAHN Analyzer, controlled both manually and by CAHN control software DCA2d Version 2.0. The instrument recorded the force in units of mg depending on the immersion depth. The resulting force values (in mg) depend on the sample geometry, which was a round glass slide with 18 mm diameter. Three to six measurements were performed per sample. The film was initially placed above the fluid and lowered into the water. The advancing force was recorded as the slide touched the water surface.

X-ray photoelectron spectroscopy: X-ray photoelectron spectroscopy was performed using a Perkin-Elmer 5400 instrument. The x-ray source was a magnesium ray of 1253.6 eV, operating at 300 watts and 14 kV. Analyses were run with a vacuum of approximately 1x10-7 torr, using a hemisperical analyzer and fixed analyzer ratio. The system was controlled by Appollo 3500 software. The incident angle was varied between 40 and 90° by tilting the sample stage. Tests were carried out to determine possible degradation of the films by x-rays and the results showed that an exposure of over 35 min resulted in degradation. All measurements were conducted with a maximum x-ray exposure of 30 min. Films were prepared as usual by pipetting 6 drops of solution onto small microscope cover slides and stored at room temperature in glass petri dishes. All glassware that was in contact with the films or solution (glass slides, petri dish and pipettes were sonicated in acetone for 20 min to remove all traces of Si contamination). The computer software provided the elemental composition (in atomic %). Deconvolution of the carbon core peaks was done using Gaussian curve fitting. The peak width at half-height was kept at 1.7 and the fitting underwent a maximum of 25 iterations. The software provided values for peak areas.

Atomic force microscopy: AFM measurements were conducted on films cast on glass slides. The films were coated with the respective solutions at room temperature and stored at 4°C until the measurements were carried out. The measurements were conducted on a Dimension 3000 Scope, controlled by a Nanoscope IIIa controller, both by Digital Instruments. Several samples using at least two different silicon nitrile tips were used per film in order to exclude artifacts. The AFM images were plotted at a color contrast of –4 and a color offset of 26.

Results and Discussion:

1. Static contact angle measurements:

Neat and blended films containing various fluorine (F)-containing random copolymers (Table I) were subjected to wetting force measurements using a modified Wilhelmy plate method. The measurements were to assess the surface free energy of the films, which is expected to give an indication of the surface segregation process. The force that is acting on the film when it is dipped into the examining liquid, in this case water, is measured. For all blends examined, the principal behavior is a rapid decline in wetting force at low blend concentrations of the F-ester (Figure 1) and this behavior has been reported previously[17]. At low blend concentration, the rapid decline in wetting force was explained with surface segregation of the F-ester in the blend. This result was expected, since it is commonly observed that in blends of a hydrophilic and a hydrophobic species, the hydrophobic material migrates to the surface in order to minimize the surface free energy of the system. The decline is seen to become less dramatic at higher concentrations, and at concentrations above 30-50% blend concentration the blended films showed a wetting force in the order of the force observed for neat films (100% F-ester) (Figure 1). An identical wetting force indicates a chemically identical surface composition and this signifies that at blend concentrations above 30-50% the surface consists essentially of pure F-ester.

The wetting forces observed on neat films were found to depend on the type of F-containing substituent groups, and they varied between –13 and –38 mg (Figure 2). The lowest wetting forces were observed for the F-esters with CF_3 terminal functional groups and the forces registered for F-esters with CF_2H terminated F-esters were generally higher, independent of the total F-content of the sample (Figure 3). This behavior shows that the wetting force is not only dependent on the F-content, but also on the specific type of F-group present. This can be explained with the presence of a lone proton at the terminus of the CF_2H-endgroup. The proton is electron deficient, which renders it acidic. It therefore can interact with other polar molecules like, for example, water by hydrogen bonding. Because of this proton, all difluoromethane-terminated end-groups have higher wetting forces than the corresponding trifluoromethyl-terminated derivatives, regardless of overall F-content.

2. XPS measurements:

The five different fluorine-containing random cellulose ester derivatives (Table I) were analyzed with regard to their fluorine content by elemental composition, ^{1}H-NMR spectroscopy, and XPS. The determinations by XPS involved both powderous and solvent-cast film samples. The results indicate satisfactory agreement between the F-determination by solution NMR and by XPS as powder. The results are thought to be within the experimental error for XPS measurements at a 45^{o}-incident angle. However, F-content determinations using solvent cast films reveal in part significant discrepancies (Table II). These differences, which are significant and reproducible, suggest surface organization as discussed below.

XPS measurements on solvent cast films having variable fluorine-containing cellulose ester content were carried out using the typical incident angle of 45^{o} as well as others. Survey scans revealed the presence of carbon, oxygen and fluorine in all films containing F-esters; and they revealed only carbon and oxygen in the control film consisting of neat CP. Deconvoluting the carbon peaks according to different types of carbon bonds present using the XPS software permitted the distinction of C-F bonded atoms from those having other bonding patterns (Figure 4). Since the areas of the peaks can be calculated using the XPS software, the ratio of the peak areas of two specific types of carbon atoms, the CF_3 to CH_3 ratio, could be determined and used for assessing the presence of F-atoms at the surface. For all blended systems, the experimentally determined CF_3/CH_3-ratio was found to be larger than the theoretical one, which was calculated according to blend composition. This indicates that there is a higher F-content on the surface of blended films, i.e., surface segregation has occurred. This is in agreement with the results obtained by static wetting force measurements. The ratio between the experimental and theoretical CF_3/CH_3 ratio is empirically defined as the segregation factor (SF) which gives an indication of the extent of surface segregation. The segregation factor determined using blends containing 1% F-ester was used to assess differences in segregation behavior for the different F-containing cellulose ester preparations (Table III). The segregation factor was found to be highest for the hydroxy-functional F-ester, and it was lower for all peracylated F-esters (Table III).

When cellulose ester films with increasing F-ester content were examined by XPS at 45^{o} incident angle, a declining segregation factor with declining F-ester content was observed (Figure 5). The observed decline agreed with the force data (Figure 1), which showed the sharpest decline in wetting force at lowest F-ester content.

In addition to F-ester content, surface segregation was found also to depend on the elemental F-content of the F-ester blended. The segregation factor was found to increase after an F-content of the F-ester of 10% and was independent of the F-content between F-contents of 10 an 30 %, after which the segregation factor increased once more(Figure 6). This is in accordance with literature reports, where this behavior was explained with a threshold behavior[21]. The F-content represents the difference in hydrophobicity of the two components, and only after a certain difference is reached, increased surface segregation is observed. for a variety of systems.

3. Angle dependent XPS measurements:

Blends: XPS measurements with varying incident angle are capable of probing the surface at variable depths. The incident angle of XPS measurements can easily be changed by tilting the sample. Typically, the CF_3 / CH_3 ratio decreases in an exponential fashion as the incident angle increases. The plot can be linearized by relating the incident angle to the sampling depth and X-ray energy (Figure 7). The slope of the curves signify the decline the CF_3/CH_3 ratio per distance from the surface (i.e. increasing sampling depth). The change in the CF_3/CH_3 ratio was normalized to the theoretical CF_3/CH_3 ratio (i.e. at 45° incident angle) in order to adjust for different F-contents depending on the type of F-ester used and its content in the blend. The normalized ratio was found to decline with increasing sampling depth, for all blend concentrations, independent of type of F-ester (Figure 8). This behavior is explained with surface segregation of F-containing species. If there is only a limited reservoir of F-containing species (as in blneds with low F-ester content), there must also be a greater depletion of F towards the interior of the film. The depletion, i.e. the sharpness of the decline in the normalized ratio, was found to depend on the blend content of the F-ester. For every type of F-ester, the depletion was stronger at lower blend content and became weaker at higher blend contents of the F-ester. This is explained with the fact that a stronger surface segregation occurs in blend with low content of F-ester. The stronger the surface segregation is, the larger is the proportion of the available F-ester that resides at the surface, depleting the total F-reservoir. As a result, the depletion of the F-species towards the bulk phase is stronger.

Neat films: The segregation factor was also determined for neat (100%) films of the F-esters. Contrary to the segregation factor in blended systems, the factor was below 1 for all neat films (see Table II). This indicates the absence of surface segregation and even a surface deficiency of the F-containing species. In neat films complete segregation of F-esters cannot take place, because it is only a one-component system. But the amphiphilic F-esters have hydrophobic and hydrophilic domains, and internal, intramolecular segregation can occur. Internal arrangements in neat films are thought to cause the apparent F-deficiency. However, the XPS observation is in direct contradiction to the wetting force measurements, which reveal that the lowest forces, i.e. the most hydrophobic surfaces, are observed in neat films. The wetting force measurements show that F-atoms are located at the surface, but they are not registered by XPS measurements. This is attributed to the fact that the wetting force measurements assess the first 5-10Å of the surface, whereas XPS measurements at 30° incident angle measure at a nominal sampling depth of 31Å. It is therefore possible that there is a monolayer formation of F-containing molecules at the outermost surface, which is not detected by XPS, since its detection depth already exceeds the dimension of self-organization. However, the monolayer can be measured by wetting force measurements, due to their sensitivity to the outermost surface.

4. AFM measurements:

Phase image AFM measurements were conducted in order to determine surface heterogeneities in blended films containing CP and an F-ester. Phase image AFM measures the softness of the surface, and if two phases have sufficiently different surface softness, the different phases can be detected by AFM. Of all the examined samples (see Table I), only blends containing S-CF_2H-1.5-ac showed two distinct phases at the surface (Figure 9 a-d). This is explained with the damping characteristics of the materials having T_g's near ambient.

S-CF_2H-1.5-ac has the lowest T_g and it possibly provides enough contrast in softness compared to CP for two phases to be detected by AFM. The corresponding height image revealed that the minor phase (the phase with the lower phase shift) corresponded to height features (Figure 10). The lower phase shift can consequently be caused by a different phase or it can be reflective of the height differences. As an alternative, the protrusions seen in the height image can correspond to the minor phase, i.e. the minor phase resides elevated on the matrix. This is reminiscent of lens-shaped domains seen on surfaces of blended systems[22,23]. The minor phase is initially hypothesized to be the F-ester phase, since it has the lower blend concentration.

The amount of the minor phase, indicating the F-ester phase, increased with increasing blend concentration of the F-ester up to a blend concentration of 10%. At higher blend concentrations, only one phase was detected. This is thought to indicate a monolayer of the F-containing species at blend concentrations in excess of 10%. The area occupied by the minor phase was calculated using image analysis, technique it was compared to the blend concentration of the F-ester (Figure 11). It indicates surface coverage of the F-ester at concentration above 10%. The result agrees well with XPS measurement in which, at 10% blend concentration, the detected F-content was found to be similar to the theoretical one for pure S-CF2H-1.5-ac (Figure 11). This strengthen the hypothesis that the F-ester phase resides on top of the matrix.

Conclusions:

Contact angle measurements and XPS data indicate that surface segregation takes place in blends containing F-esters. The wettability of neat films of random copolymers does not only depend on the F-density of the F-containing group, but also on the type of terminus. CF_2H terminated esters have higher wetting forces and this is attributed to the interaction of the lone proton with the wetting liquid.

The amount of surface segregation in blends containing F-esters was found to depend on the total amount of F in the F-ester. Surface segregation results in a depletion of F-content towards the bulk phase.

XPS measurements of neat films of F-esters indicate a surface deficiency of F, although wetting force measurements indicate highest presence of F at the surface in neat films. These contradictory results are explained by an internal segregation of hydrophobic and hydrophilic moieties in neat films, resulting in a monolayer of F at the outermost surface.

AMF measurements revealed surface heterogeneities and supported the concept of monolayer formation.

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Table I: List of statistical F-esters used in this study

Designation	Type of ester group	Terminus in ester group	DSF[5]	Other substituent	T_g[6]
S[1]-CF_3[2]-1.5[3]-ac[4]	Trifluoro ethyl	CF_3	1.5	Acetyl	
S-CF_3-1.0-ac	Trifluoro ethyl	CF_3	1.0	Acetyl	130
S-CF_2-1.0-ac	Difluoro ethyl	CF_2H	1.0	Propionyl	66
S-CF_2H-1.5-ac	Octafluoro pentyl	CF_2H	1.5	Propionyl	53
S-CF_2H-1.5-OH	Octafluoro pentyl	CF_2H	1.5	OH-functional	113

[1] denotes statistical distribution of F-ester groups along the cellulose backbone
[2] denotes type of terminus in ester group
[3] denotes DS_F
[4] denotes type of substituent not esterified with an F-group: OH indicates free hydroxyls, ac indicates acylated hydroxyls (non F-containing ester)
[5] calculated from elemental analysis data or NMR results
[6] determined by DSC

Table II: Comparison and properties of neat statistical copolymers

Sample[1]	F-content, %			SF[5]
	theoretical[2]	by XPS of powders[3]	by XPS of films[4]	
		at 45° incident angle		
R-CF2H-1.5-OH	32	29	20.87	0.56
R-CF2H-1.5-ac	28	28	7.9	0.27
R-CF3-1.5-ac	15.2	13	10.25	0.91
R-CF3-1.0-ac	11.54	8.8	11.09	0.73
R-CF2-1.0-ac	9	7.8	5.28	0.65

[1] for sample designation, see Table I

[2] calculated from NMR or elemental analysis

[3] measured on powderous F-esters at 45° incident angle as % F (atomic), excluding H

[4] measured on solvent-cast (THF), neat films, (100%), F-esters at 45° incident angle as % F (atomic), excluding H

[5] Surface segregation factor, calculated from theoretical and experimental CF_3/CH_3 ratio in neat films (see also text)

Table III: Characterization and properties of blended films containing 1% F-esters

Sample[1]	CF_3/CH_3 ratio[2]		SF[5]
	theoretical[3]	experimental[4]	
R-CF2H-1.5-OH	0.015	0.155	10.37
R-CF2H-1.5-ac	0.02	0.11	5.38
R-CF3-1.5-ac	0.005	0.023	4.60
R-CF3-1.0-ac	0.002	0.0091	4.54
R-CF2-1.0-ac	0.002	0.0068	3.40

[1] sample designation as in Table I

[2] ratio calculated from peak areas of CF and CH peak (for deconvolution, see Figure 4)

[3] ratio calculated from blend concentration excluding H

[4] measured ratio at 45° incident angle, excluding H

[5] Segregation factor calculated from theoretical and experimental CF3/CF2 ratio in neat F-ester films.

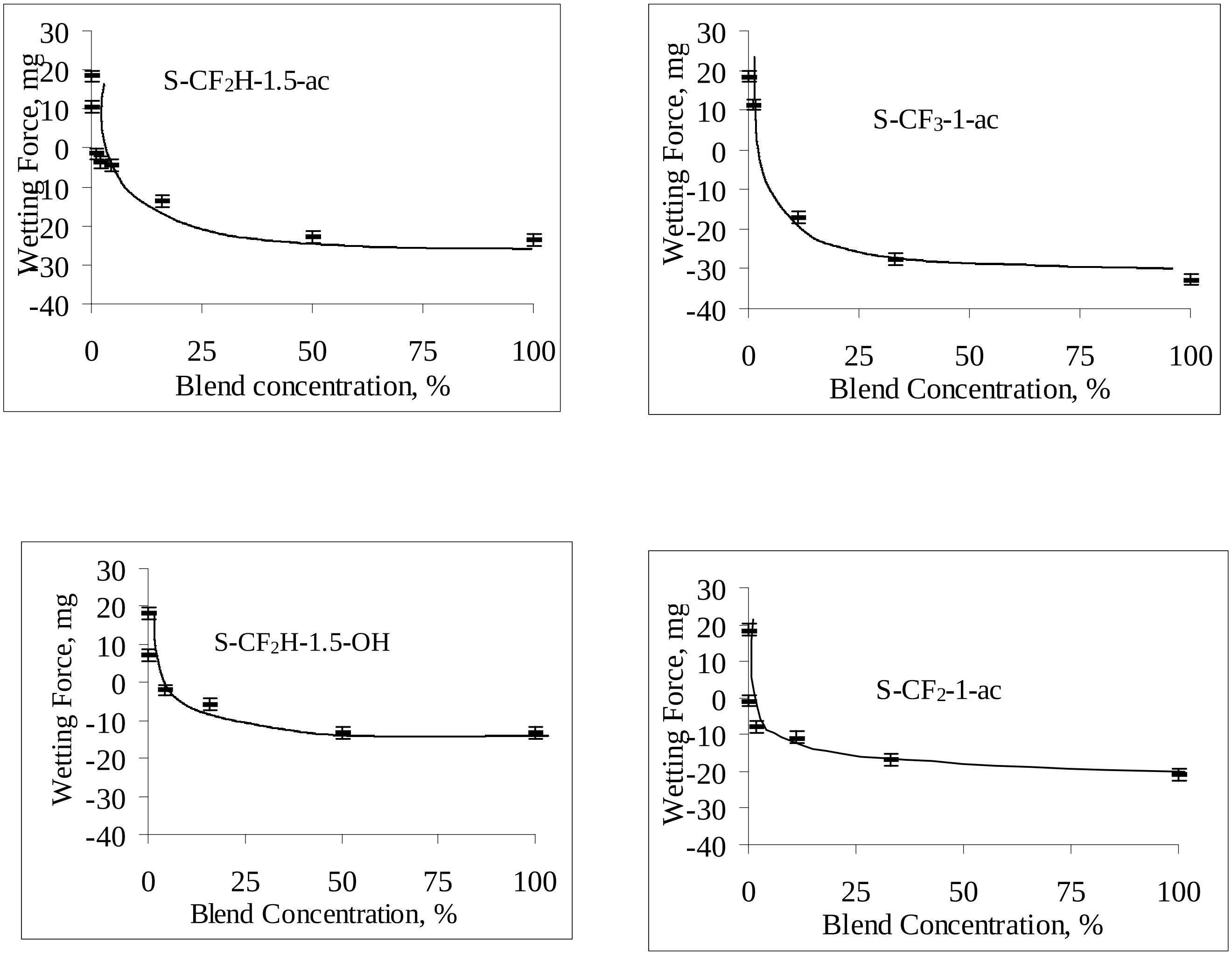

Figure 1:
Results of wetting force measurements depending on the blend content of the F-ester for four esters. The average variation of 6 repeats was ± 0.53 mg.

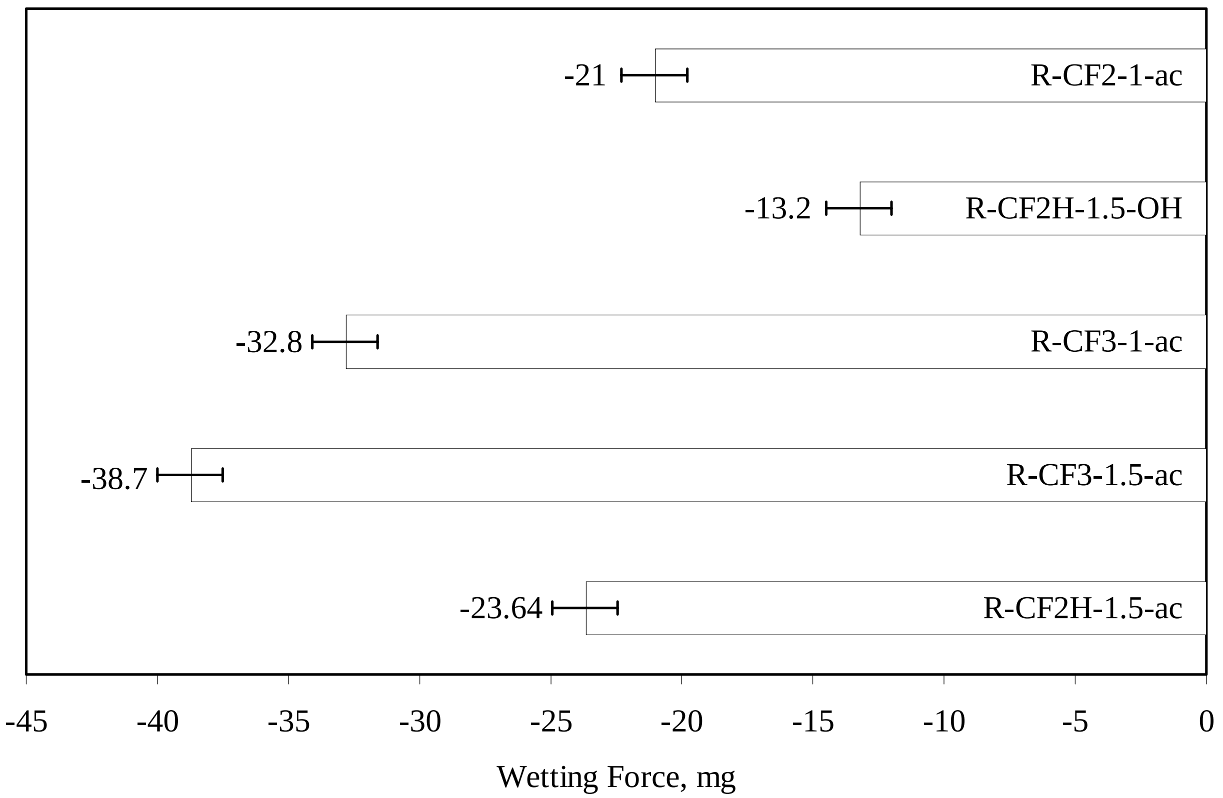

Figure 2:
Results of wetting force measurement for solvent-cast (THF) films of neat F-esters depending on the type of F-group in the ester

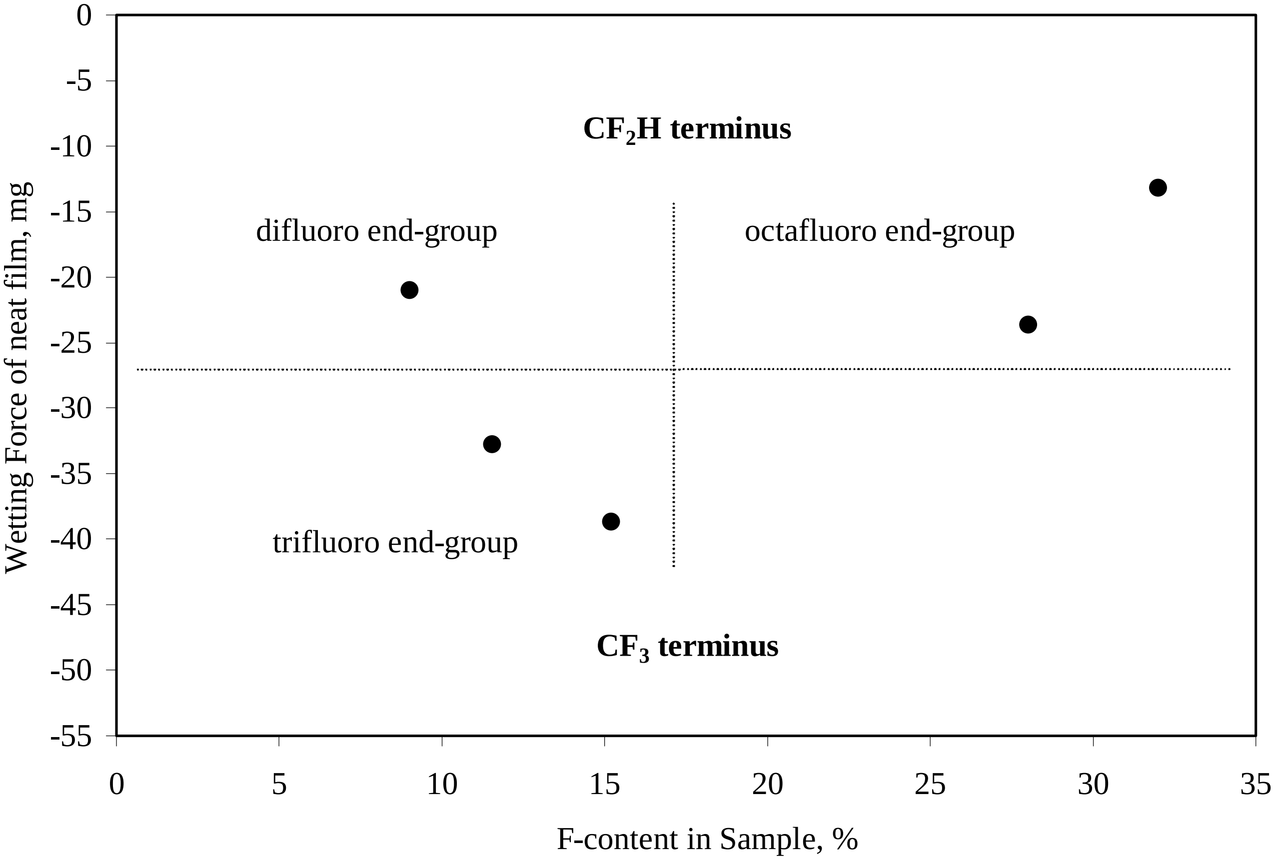

Figure 3 :
Correlation between the F-content of the F-ester and the wetting force observed in neat films. Films of the F-esters with the difluoro-terminus have a higher wetting force, independent of the F-content in the sample.

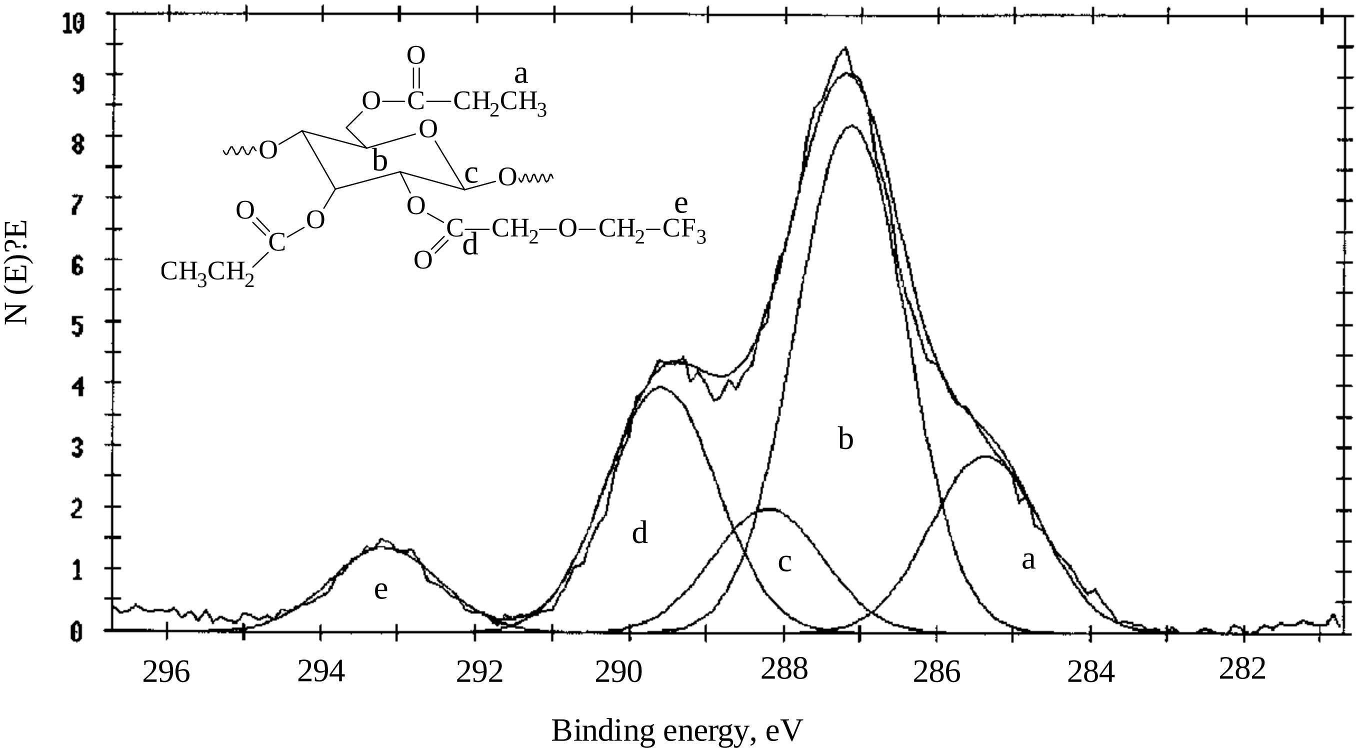

Figure 4:
Deconvolution pattern of the C1 core peak according to the different chemical environments of the various carbon atoms. The peak areas can be determined using the XPS software.

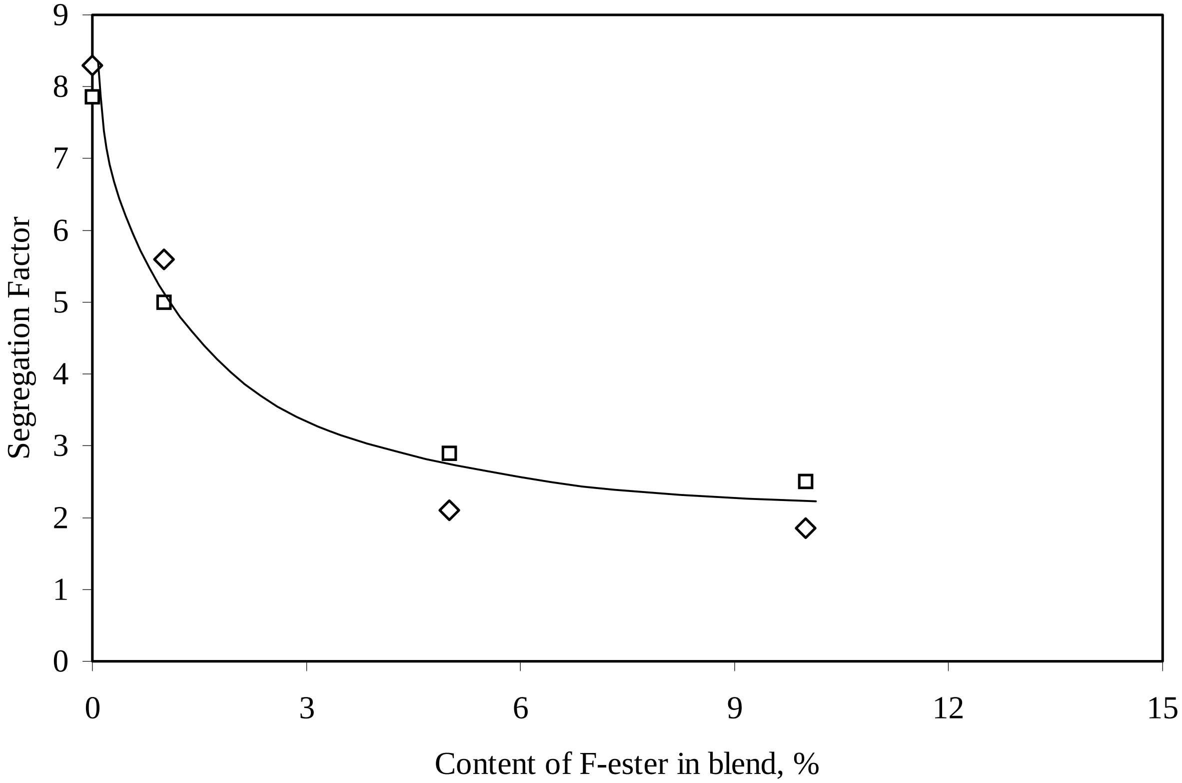

Figure 5:
Dependence of the segregation factor (SF) on the blend concentration. The highest SF is observed at the lowest blend content. The behavior is identical for all blends. The experiment was done in duplicate.

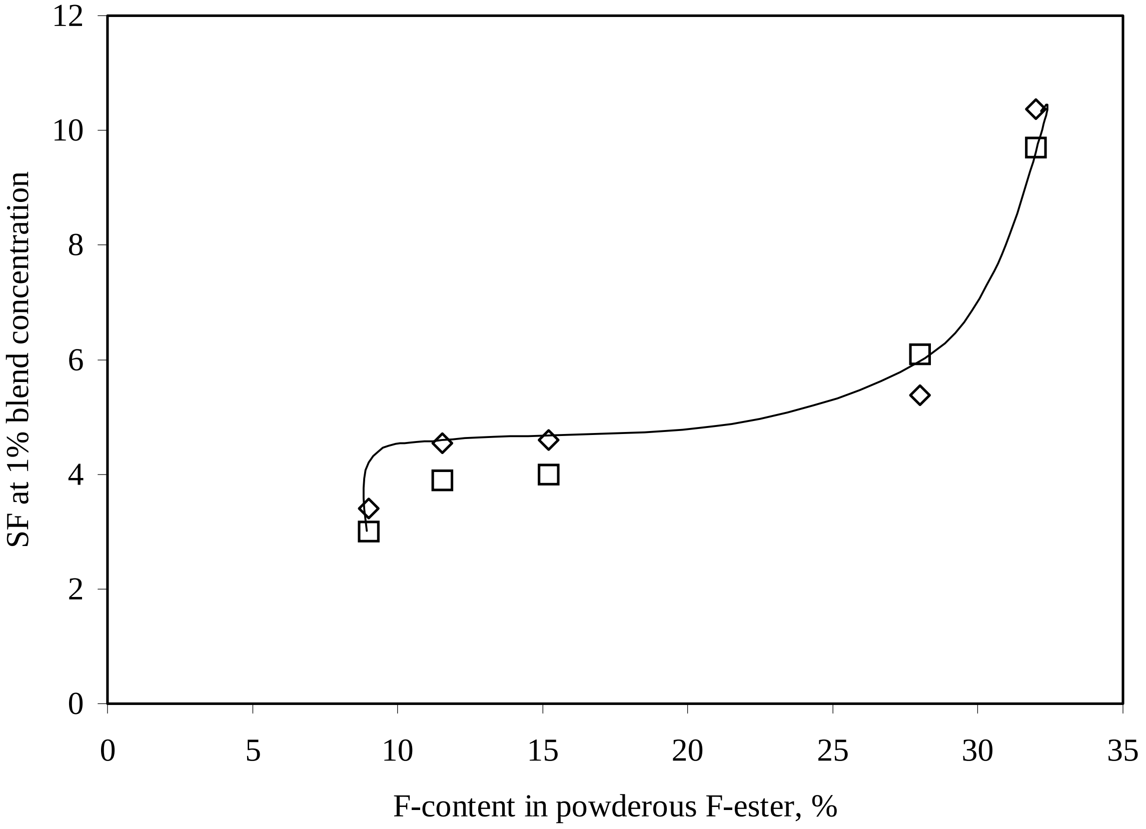

Figure 6:
Dependence of the segregation factor (SF) on the F-content in the F-ester. With increasing F-content, the amount of surface segregation increases, as indicated by a larger SF

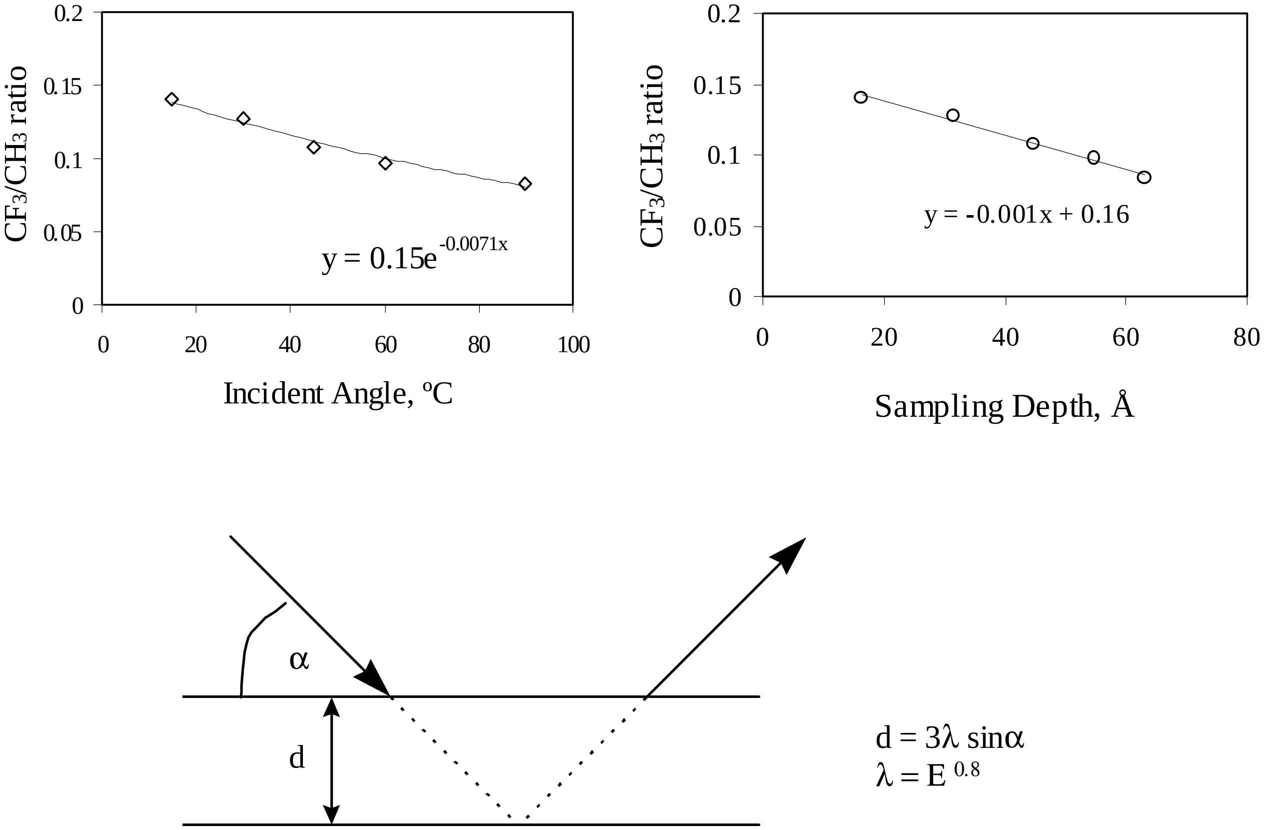

Figure 7:
Transformation of exponential F-gradient (top left) into linear profile (top right) using the geometrical relationship between escape depth and incident angle and the x-ray energy (bottom)

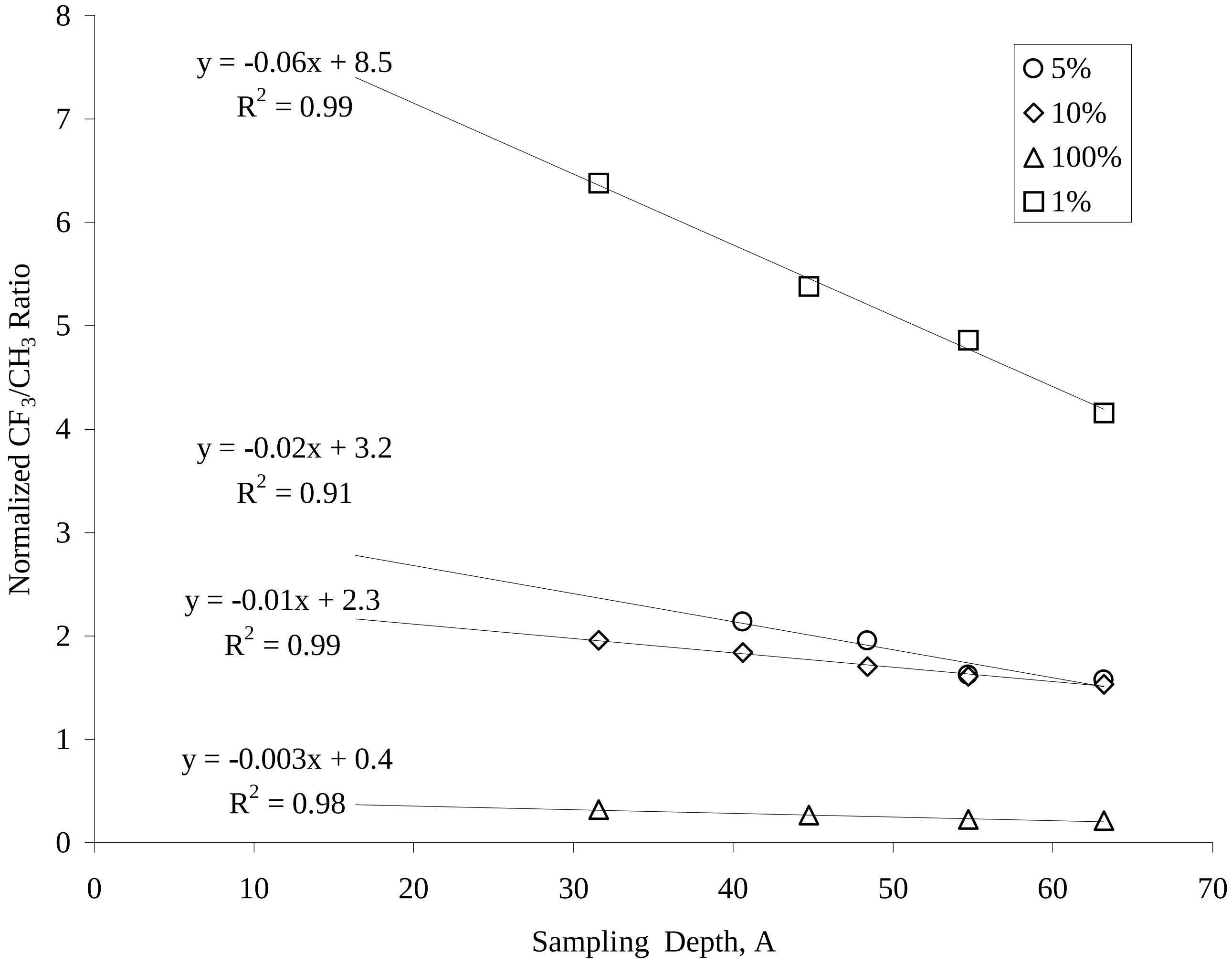

Figure 8:
The normalized CF_3/CH_3 ratio depending on the sampling depth and the blend concentration of the F-ester. The lower the blend content of the F-ester is, the more dramatic is the decline in the normalized ratio. These data were obtained from S-CF_2H-1.5-ac, and all F-esters show the same behavior.

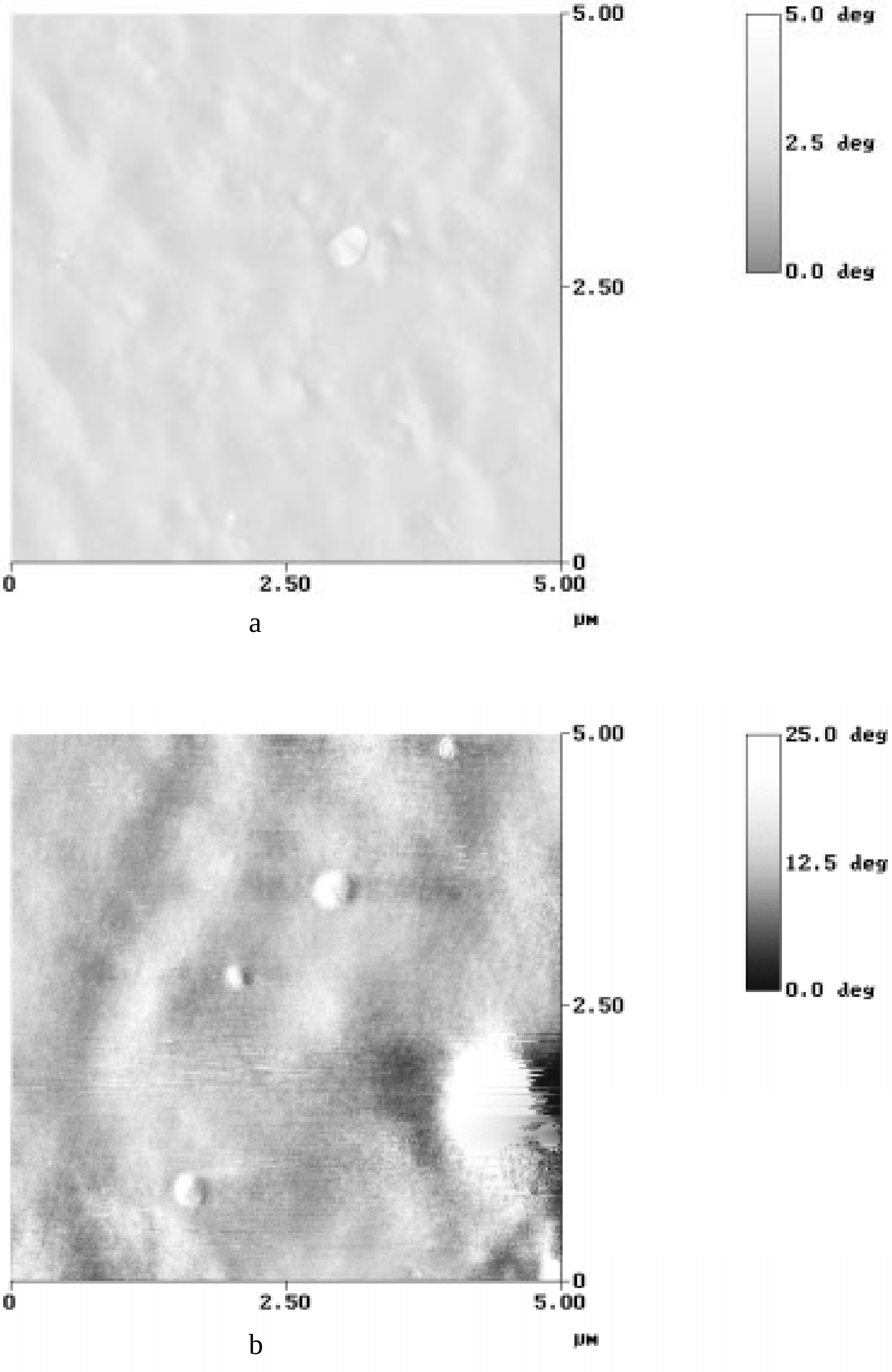

Figure 9 a,b:
Atomic force phase image micrographs of a film of 100% CP (top) and 100% S-CH_2-1.5-ac (bottom).

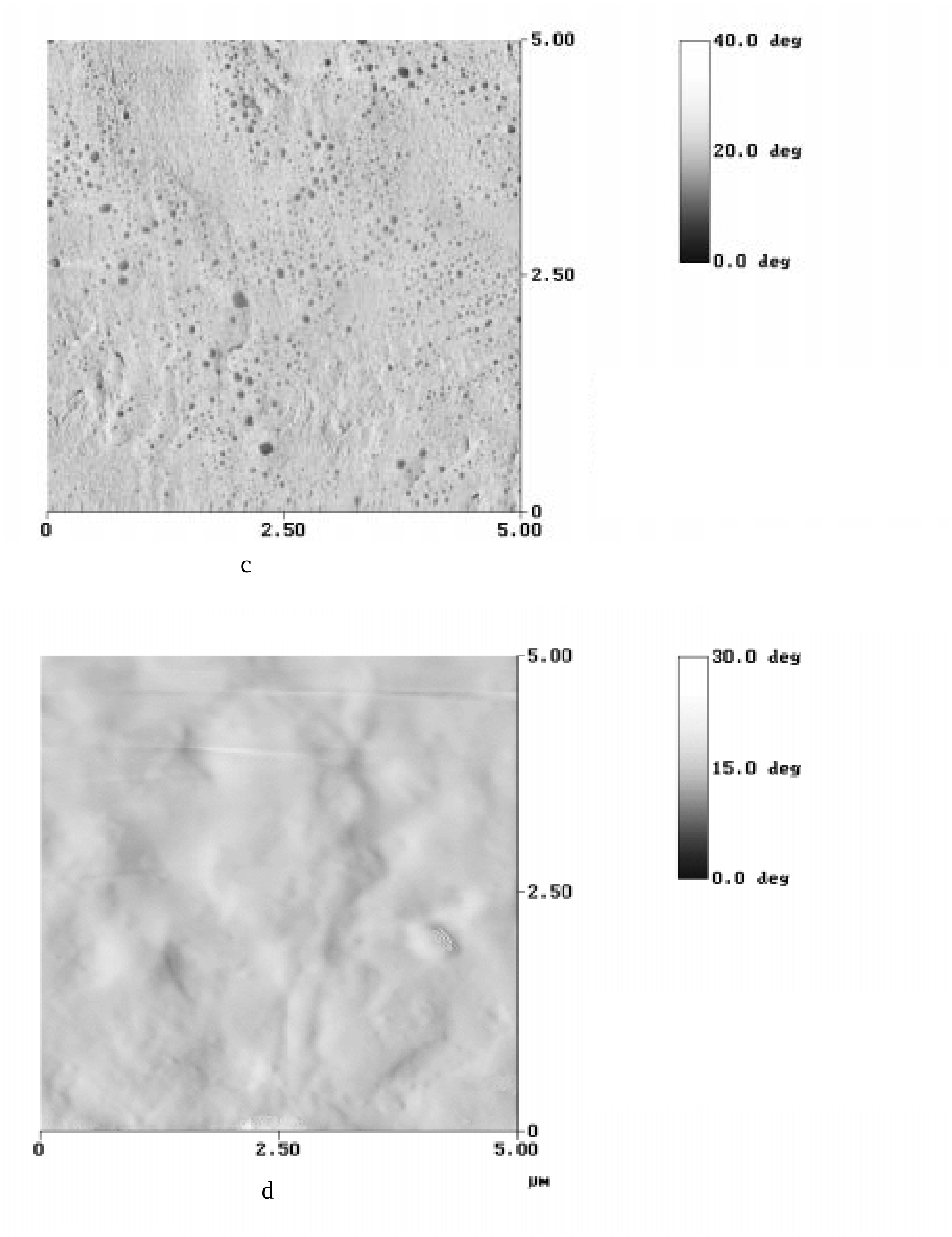

Figure 9 c,d:
Atomic force phase micrographs of a blend containing 2% S-CF_2H-1.5-ac (top) and 10% S-CH_2-1.5-ac (bottom).

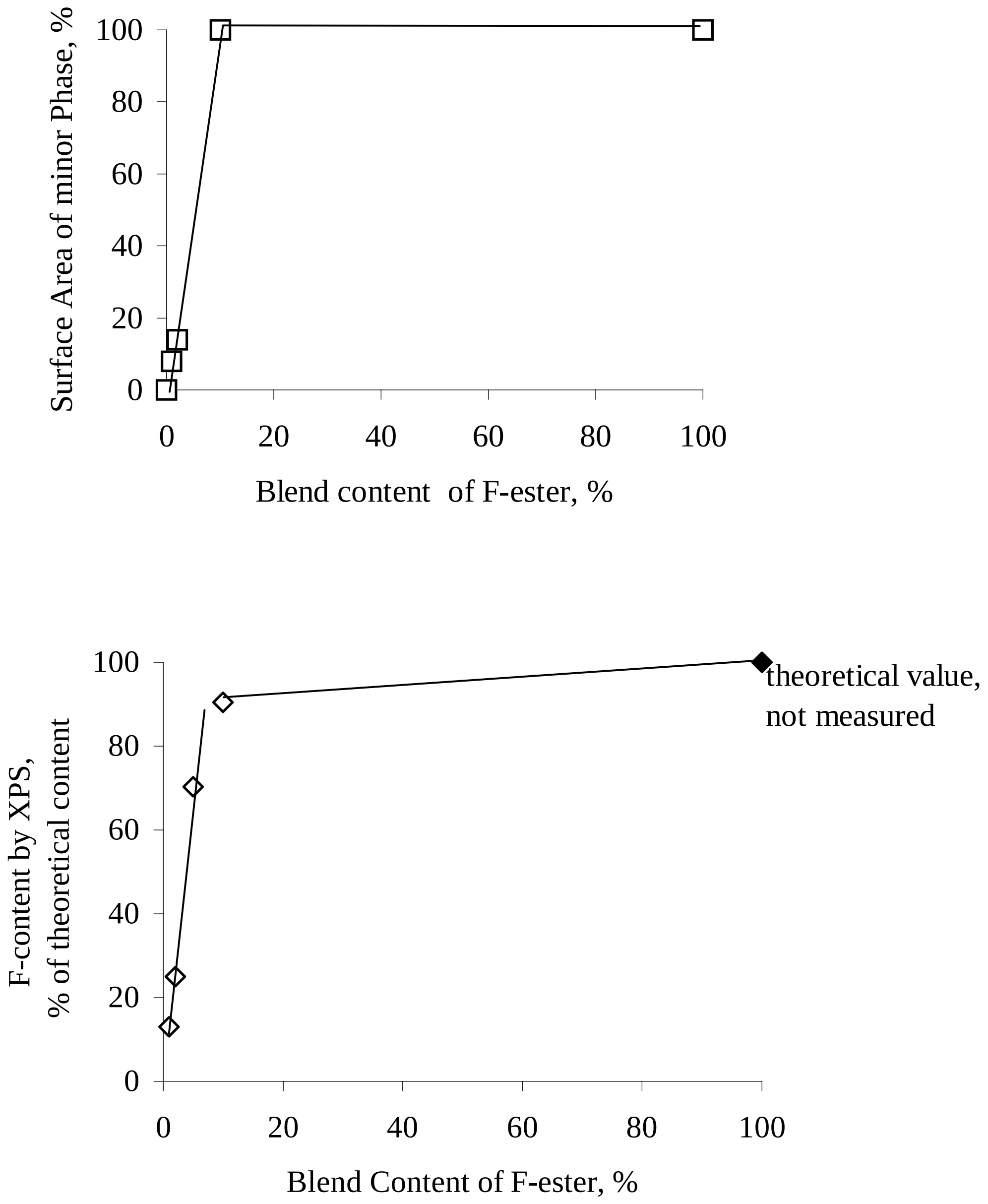

Figure 11:
Comparison of the surface coverage of S-CF_2H-1.5-ac obtained by image analysis of AFM phase image data (top) and the F-concentration measured by XPS for various blend contents of the F-ester (bottom)