Smart surfaces of biobased materials:
IV. Dynamic surface effects in films of F-containing cellulose esters

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Abstract:

Dynamic surface phenomena were examined in films of fluorine (F)-containing cellulose derivatives. The derivatives were either statistical F-esters or F-terminated segments. Dynamic wetting force measurements indicated hysteresis behavior in all films. The hysteresis depended on kinetic (water sorption and reorganization) and thermodynamic (surface roughness and surface coverage with F-moieties) factors. Consecutive force loops revealed an increase in the wetting force with increasing loop number, indicating an increased hydrophobicity of the surface. The force increase was determined to be due to water sorption as well as surface reorganization. In increase in the size of the F-groups signified a decrease in reorganization rate due to a decreased mobility of the group. The process of reorganization was fully reversible, a behavior which is congruent with the definition of smart behavior.

Introduction:

Polymeric materials find widespread applications in composites, biomedical applications, and coatings among others. In many of these applications, the surface characteristics are crucial to the performance. The characterization of the surfaces,

however, can be inaccurate since the configuration of surfaces (i.e. the actual distribution of moieties at the surface) changes with changes in the environment[1]. For example, the interfacial energy of polyurethanes is measured (under ambient conditions) to be high, indicating limited biocompatibility. Still, polyurethanes exhibit good biocompatibility, a fact that is attributed to a low interfacial energy in an aqueous environment facilitated by surface reorganization[2].

Several factors have been identified to cause the change in configuration and among these the phenomenon of reorientation (or reorganization or reconstruction) of the surface[3] has been subject of an increased number of studies[4,5]. It represents a purposeful response to the environment and as such constitutes smartness of materials. Reorganization is related to surface segregation in that in both cases the driving force is the minimization of the interfacial free energy. Commonly the change in environment constitutes the transition from the atmosphere (air, i.e. hydrophobic) into an aqueous environment. In air, the surface is comparatively hydrophobic and in water the hydrophobic groups try to move to the interior of the material, making the surface more hydrophilic.

Surface reorganization has been studied extensively, because of its theoretical and practical importance. Surface reorganization is facilitated by rotational movements in the polymer[6,7], similar to the movements detected in β and γ transitions commonly detected by thermal analysis. Whereas the principle of mobility is well established, only a few studies have been conducted with the aim of distinguishing surface mobilities depending on the size of the rotating group. An objective comparison of different mobilities of side-chain groups in polymers is difficult, since the T_g changes in many cases with the side-

chain group is varied. In these cases mobility depends on the size of the group and the T_g of the polymer[8]. Other studies showed that steric hindrance also influences mobility[9].

The detection of reorientation requires the examination of the surface in different environments, commonly air (hydrophobic) and water (hydrophilic). Wetting force measurements are ideally suited for this test. Wetting force measurements are a sensitive techniques to characterize the outermost surface of a polymer[10] and thus depend strongly on the presence or absence of functional groups, surface roughness, heterogeneity and reorganization[11]. Dynamic wetting force measurements (i.e. at a moving liquid line) yield the force hysteresis. The hysteresis is defined as the difference between the advancing and receding wetting force and it can be distinguished into a thermodynamic and a kinetic component. Thermodynamic hysteresis is derived from surface roughness and chemical heterogeneity and arises from the fact that the advancing and receding forces are measured at different positions. Kinetic hysteresis describes time dependent phenomena like sorption and reorganization.

We have recently examined the self-assembly behavior of various F-containing cellulose derivatives[12,13]. This study is to investigate time-dependent phenomena on surfaces of solvent cast films of these F-containing cellulose derivatives, with emphasis on the description of differences in the mobility of the F-containing group.

Experimental:

Materials:

Cellulose propionate was purchased from Aldrich Chemical. F-containing cellulose derivatives were synthesized in our laboratory as described previously[14,15]. They were

either statistical esters with a number of F-containing ester groups evenly distributed along the cellulose backbone or F-terminated segments of low molecular weight terminated with one F-group (Figure 1).

Methods:

Dynamic wetting force measurements: Dynamic wetting force measurements were based on a modified Wilhelmy Plate method using dip-coated microscope cover slides. These were prepared by cleaning thoroughly in hexanes, dried and subsequently dip-coated (one coat) with the solutions of the F-containing derivatives (5% solution in THF). The glass slide served as sinker to ensure that the films would submerge in the wetting liquid. The solvent was evaporated at 4°C over night and all films were stored for three days before contact angle measurements were performed. 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 depending on the immersion depth, which was not converted into contact angles. Therefore it has to be pointed out that the numerical values of the reported forces reflect the geometry of the samples, which was kept identical for all samples. Three to six measurements were performed per sample. The films were cycled at 2μm/sec for 0.1 mm in each direction.

Sorption experiments: Sorption experiments were also conducted using the Cahn Balance. The films were prepared as described above. The films were initially placed above the wetting liquid (water) and lowered into the liquid at a rate of 20 μm/sec. After

the films were submerged (3 mm) the stage movement was discontinued and the force was measured with time for 24 h.

Results and Discussion

1. Hysteresis of initial wetting force loop

Dynamic contact angle measurements of films of the F-containing cellulose derivatives (Figure 1), either terminated segments or statistical F-esters (Table I,II), were conducted using a modified Wilhelmy Plate method with water as the interrogating liquid. The experiments were conducted at an immersion/withdrawal speed of 2 μm/sec at a travel distance of 0.1 mm. The time span covered by one loop was 100 sec. Altogether, 7 loops were measured resulting in a total experiment duration of 12 min.

All films examined, either films of the F-derivatives or CP (as control), exhibited wetting force hysteresis behavior (Figure 2). Hysteresis thereby represents the difference between the advancing and receding forces, which are measured at the advancing fluid line and the receding fluid line, respectively.

The magnitude of the hysteresis was examined with regard to the chemical nature of the F-containing derivative. The derivatives differed in architecture (statistical F-ester vs. terminated segment) and F-content (type of F-group, degree of substitution of F-substituent (DS_F), CP segment size) (Figure 3). The lowest hysteresis-value of 5 mg was observed for the control film (100% CP) which was between 20 and 120% lower than the hysteresis of the F-containing films. Films containing the statistical F-ester showed hysteresis-values between 5.9 and 11.34 mg, depending on the nature of the terminus of the F-group (Figure 3). The lower hysteresis-values belonged the derivatives with the

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CF$_2$H-terminated F-groups and the higher to films with CF$_3$-terminated F-groups, the exception being the hydroxyl-containing derivative, which had the highest hysteresis.

Films containing the terminated segments, by contrast, do not show the dependence of the magnitude of the hysteresis on the terminus of the F-group (Figure 3). The hysteresis-values for all low molecular weight samples (T30-samples) are higher than the values for the corresponding F-esters (containing the same F-group) whereas the high molecular weight segments (T70-samples) have a lower hysteresis value (Figure 3) than the F-esters. Although hysteresis is detected in all films, not clear dependency on the architecture of the F-derivative or the type of F-group could be detected.

Hysteresis can be due to a number of factors. Thermodynamic hysteresis is indicative of surface roughness and different degrees of surface coverage of the low surface free energy component (in this case the F-derivative) whereas kinetic hysteresis is related to sorption and reorganization phenomena.

In order to determine the potential influence of *surface roughness* on the hysteresis the surface topology of the samples was determined by atomic force microscopy. AFM height imaging of films of F-terminated oligomers and F-esters demonstrated that the F-ester films are slightly wavy, but overall smooth. The same can be said about the control film (100% CP). However, the films of F-terminated segments are rough (Figure 4) and this has previously been attributed to the formation of solid state micelles[10]. Films containing low molecular weight segments were rougher (i.e. have dome-like protrusions at shorter intervals) then the ones with high molecular weight segments.

Partial dissolution of any F-species during the experiment will lead to a change in coverage with the F-derivative (*F-coverage*) and could also be responsible for the observed hysteresis. Especially the terminated segments show a potential for water solubility due to their low molecular weight and low F-content (see Table I). However, hysteresis is also observed in films of high molecular weight F-esters. Due to their high molecular weight and high F-content (see Table II) the F-esters are not considered to be water soluble, indicating that partial dissolution is unlikely. In addition, exploratory GC experiments of water samples in which a film of a terminated segment was submerged for 24 hrs (compared to the loop duration of 100 sec) did not show any identifiable contamination and the wetting forces of the water before and after the long term submersion were identical, indicating that the water was not contaminated.

Surface reorganization is a common phenomenon in polymer films and indicates a change in surface composition due to rotational movement of side-chains of surface molecules. Flexible ether linkages are found in the F-esters and F-terminated segments (Figure 5). Rotation around these ether linkages are considered to be the most plausible explanation for reorientation. F-containing groups that are located at the surface under dry conditions are thought to rotate into the interior of the film when the film is immersed into water. The absence of hydrophobic F-groups renders the film more hydrophilic.

The mechanism of the mobility of the OH-containing sample is slightly different: not only reorient the F-containing groups as described above, but also the OH-groups which are initially in the interior of the film orient towards the surface in water. The hydrophilicity of the film is increases by the absence of hydrophobic F-groups and at the same time by the presence of OH-groups.

Cellulose derivatives are well known for their hydrophilicity, which is mediated by the presence of multiple oxygen atoms, even in the absence of free hydroxyls. It is therefore likely that *absorption* of water occurs during the dynamic wetting force measurements.

2. Sorption experiments

Sorption measurements were conducted to determine the extent of possible sorption during wetting force measurements. Sorption was measured by submerging the film into water and measuring the force change over time at constant immersion depth (i.e. stationary liquid line). In the case of water sorption, the film becomes heavier and the force increases.

All samples show a linear increase in the wetting force with increasing duration of the experiment. At a duration of 12-14 h the force reaches a constant value for the remainder of the experiment (Figure 6). The increase is thought to be indicative of water absorption and the constant force after 12-14 h of the experiment is due to saturation of the film.

The initial increase can be fitted to a linear expression and the slope values are an indication of the amount of weight gain per time interval. The value did not show a significant dependence on the nature of the film (Table III). All slope values for the F-derivatives as well as for the control experiment (CP) were of the order of $2\mu g\ s^{-1}$.

3. Consecutive loops

Since it is not possible to positively identify reorganization behavior by examining the hysteresis data, wetting force experiments with consecutive loops were conducted. The experiments involved 7 loops.

For all films, the advancing and receding forces increased with increasing number of loops. The difference in force was small for CP over the whole range of the experiment and considerably larger for all films of the F-derivatives (Figure 7) during the first 3-4 cycles, corresponding to an experiment duration of 300-400 sec. After that, the force difference became gradually less pronounced. The force difference is not affected by surface roughness or F-coverage, since it is always measured at the same position. Therefore it can be used to investigate sorption and reorganization. The increase of the force was compared to the data obtained from the sorption experiments in order to determine the contribution of sorption to the force change. This can only be a first approximation, since the sorption data were obtained at a resting fluid line, whereas the wetting force loops are measured at moving liquid lines. In the case of CP, 100% of the force change corresponded to the weight gain due to sorption (see Table III).

The films of the F-derivatives, in contrast, have a force change which is greater than the weight gain that can be attributed to sorption (Figure 8, Table III). The additional amount of force change beyond the change due to sorption is thought to be reflective of surface reorganization. The decrease in the force change with increasing loop number is thought to be reflective of a decreased amount of reorganization, while sorption is still occurring. Contribution of surface reorganization due to the increase in force was found to vary with the type of F-derivative (Table III).

A large contribution can be related to the hydrophobicity or the rate of reorganization of the reorganizing group. The rate of reorganization is related to the mobility of the groups involved and literature reports indicate that larger groups are less mobile. However, the mobility depends also on the molecular mobility, as indicated by the T_g. In the case of the F-esters, the T_g changes with the type of F-group (see Table II). It is therefore in this case not possible to rigorously relate F-group mobility to size.

However, the T_g's of all segments are similar, and in this case the mobility can be determined depending on the size of the F-group. The largest contribution to the total force change by surface reorganization (92%) is seen for the case of S-CF$_2$H-1.5-OH, and this is attributed to the presence of free hydroxyl groups. Hydroxyl groups are both, hydrophilic and mobile and their effect compounds the mobility of the F-group which moves in the opposite direction.

The contribution in the other F-derivatives (without free hydroxyls) were found to be 58 and 69% for S-CF$_2$H-1.5-ac and S-CF$_3$-1.5-ac, respectively (Table III).

It is not possible to determine if the difference in force change arise from differences in hydrophobicity or differences in mobility. A smaller force change is reflective of either a less hydrophobic group or a less mobile group. The octafluoro group is less hydrophobic which can explain the comparatively low force change. The mobility of the group in relation to its size, however, cannot be determined since both, group size and T_g change simultaneously.

The terminated segments exhibit the same T_g and therefore the mobility of the F-group is directly linked to its size. The force change decreased from the trifluoro-group to the perfluoro-group and the octafluoro-group (Table III). The perfluoro-octyl group

should affect the highest change in surface energetics because it is the most hydrophobic of the three endgroups. But its force change is smaller than that of the trifluoro group. This is thought to be reflective of a reduced mobility due to the larger size of the group.

4. Repeat measurements

As a smart process surface reorganization is expected to be reversible and repeat measurements were conducted in order to determine the reversibility of the observed force change. This was done by measuring seven consecutive loops of a given sample, drying it over night and repeating the measurement. For the repeat measurement, the advancing and receding forces were found to increase with increasing loop number in the same fashion as previously observed for the original experiments. Furthermore, the advancing force of the first loop of the repeat experiment was found to be identical to the advancing force of the first loop of the original experiment (within experimental error) (Figure 9), indicating that the initial surface configuration was regained after drying. This shows the complete reversibility of the sorption and reorganization phenomena. During the drying process, water is desorbed and the F-containing moieties orient back to the surface. The re-reorganization is facilitated by the hydrophobic environment (air) the sample encounters during the drying.

Conclusions:

Films of F-derivatives exhibit typical hysteresis behavior.

Sorption experiments reveal that sorption occurs in all film examined.

Consecutive wetting force loops indicate a force increase that is identical to the weight gain expected from sorption for CP. In films of F-esters, however, the force

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increase was greater than calculated from sorption. The difference was explained with the occurrence of surface reorganization of F-groups in the F-containing films. The rate of reorganization is related to the mobility of the F-group in the case of terminated segments.

The reorganization was found to be reversible indicating the films are smart materials.

Acknowledgements:

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Table I: Overview of terminated segments

Sample designation	DP of CP Block[1]	F-group type	Number of F-atoms in substituent	F-content (%)[2]	CP mass per endgroup (g/mole)[3]	$T_m^{4,}$ °C
T_{15}^5-TF^6	15	Trifluoro	3	0.87	4950	231
T_{15}-PF	15	Perfluoro	13	3.63	4950	231
T_{15}-OF	15	Octafluoro	8	2.29	4950	231
T_{30}-TF	30	Trifluoro	3	0.45	9900	238
T_{30}-PF	30	Perfluoro	13	1.91	9900	238
T_{30}-OF	30	Octafluoro	8	1.19	9900	238
T_{70}-TF	70	Trifluoro	3	0.18	23000	242
T_{70}-PF	70	Perfluoro	13	0.78	23000	242
T_{70}-OF	70	Octafluoro	8	0.48	23000	242

[1] calculated from molecular weight data
[2] calculated as atomic % of F-atoms on all atoms of the sample, excluding protons
[3] calculated from GPC data
[4] determined by DSC
[5] indicates DP of CP block
[6] indicates type of end-group

Table II: Characteristics of statistical F-esters

Designation	Type of ester group	Terminus in ester group	DS_F[5]	F-content, %[6]	other substituent	Tg[7], °C
S[1]-CF_3[2]-1.5[3]-ac[4]	Trifluoroethyl	CF_3	1.5	15.2	acetyl	
S-CF_3-1-ac	Trifluoroethyl	CF_3	1.0	11.5	acetyl	130
S-CF_2-1-ac	Difluoroethyl	CF_2H	1.0	9	propionyl	66
S-CF_2H-1.5-ac	Octafluoropentyl	CF_2H	1.5	28	propionyl	53
S-CF_2H-1.5-OH	Octafluoropentyl	CF_2H	1.5	32	OH-functional	113

[1] denotes statistical F-ester architecture
[2] denotes type of terminus in ester group
[3] denotes DSF
[4] denotes type of OH which are not esterified with the F-group: OH indicates free
  hydroxyls, ac indicates esterified hydroxyls (non F-containing ester)
[5] calculated from elemental analysis data or NMR results
6 calculated from NMR data or elemental analysis
[7] determined by DSC

Table III: Comparison force increase calculated from to weight gain by sorption and measured in wetting force experiment

Sample[1]	Slope Factor[2] gs^{-1}	Weight Gain per 100 s, g[3]	Force Increase per 100 s, g[4]	Contribution to force increase, %	
				sorption	reorganization
CP	0.0025	0.2	0.2	100	0
T30-OF	0.0032	0.32	1	32	68
T30-TF	0.0035	0.35	2	17	81
T30-PF	0.0021	0.21	1.5	13	87
T30-OF	0.0026	0.26	1	26	74
T30-TF	0.0038	0.38	2	17	81
T30-PF	0.0018	0.18	1.5	12	88
S-CF2H-1.5-OH	0.0033	0.33	4	9	91
S-CF2H-1.5-ac	0.0042	0.42	1	42	58
S-CF3-1.5-ac	0.0046	0.46	1.5	31	69

[1] sample identification as outlined in Table I
[2] from sorption plot (see Figure 6)
[3] calculated from slope value
[4] determined in wetting force experiment
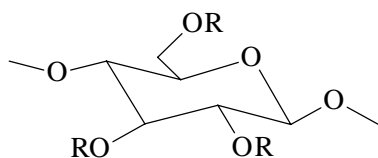
where R = CO-CH$_2$-O-CH$_2$CF$_2$H (difluoro)
= CO-CH$_2$-O-CH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H (octafluoro)
= CO-CH$_2$-O-CH$_2$CF$_3$ (trifluoro)

with DS of 1-2, remaining R = H, CO-CH$_2$-CH$_2$
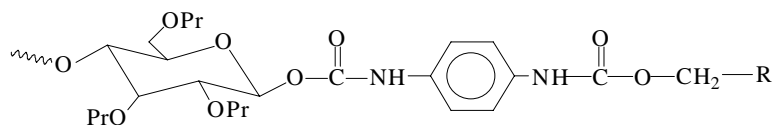
where R = - CF$_3$ (trifluoro)
- CF$_2$CF$_2$CF$_2$CF$_2$H (octafluoro)
- CH$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_3$ (perfluoro)

Figure 1:
Structures of F-derivatives used in this study. Top: statistical F-ester, bottom: terminated segments
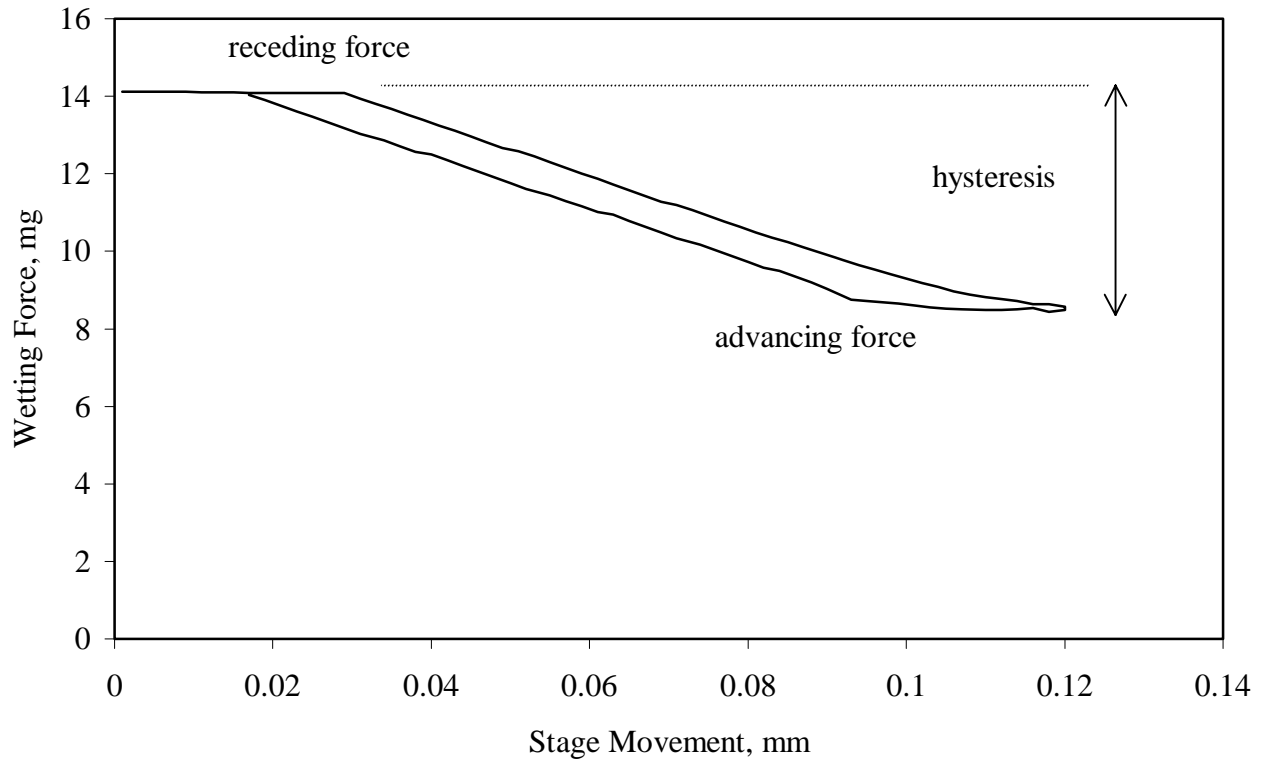
Figure 2:
Typical trace of first wetting loop. The hysteresis is calculated from the
difference between the advancing and receding forces.
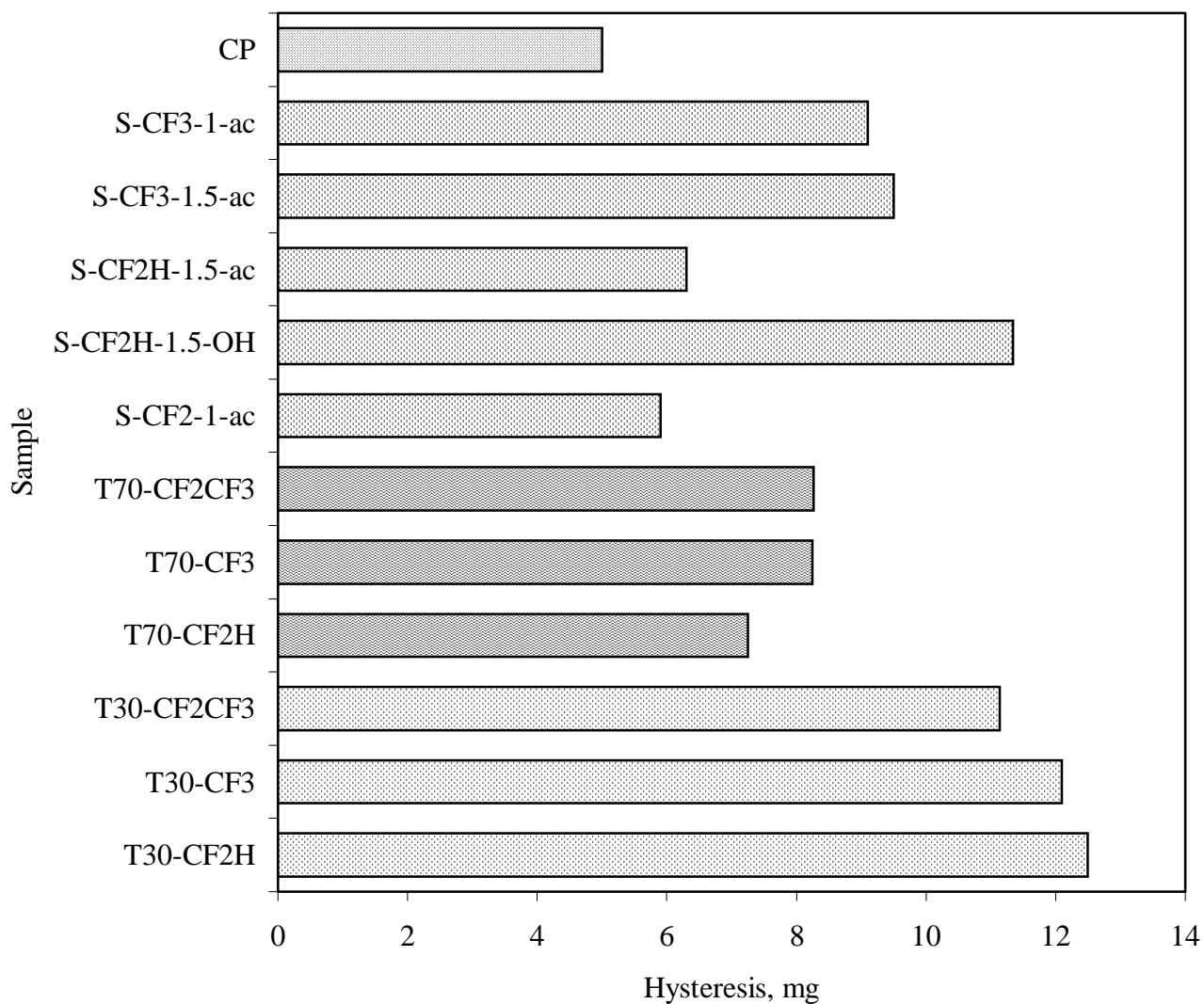
Figure 3 :
Hysteresis-values for films of F-esters and F-terminated segments with different
F-containing groups (for sample designation see Table I).
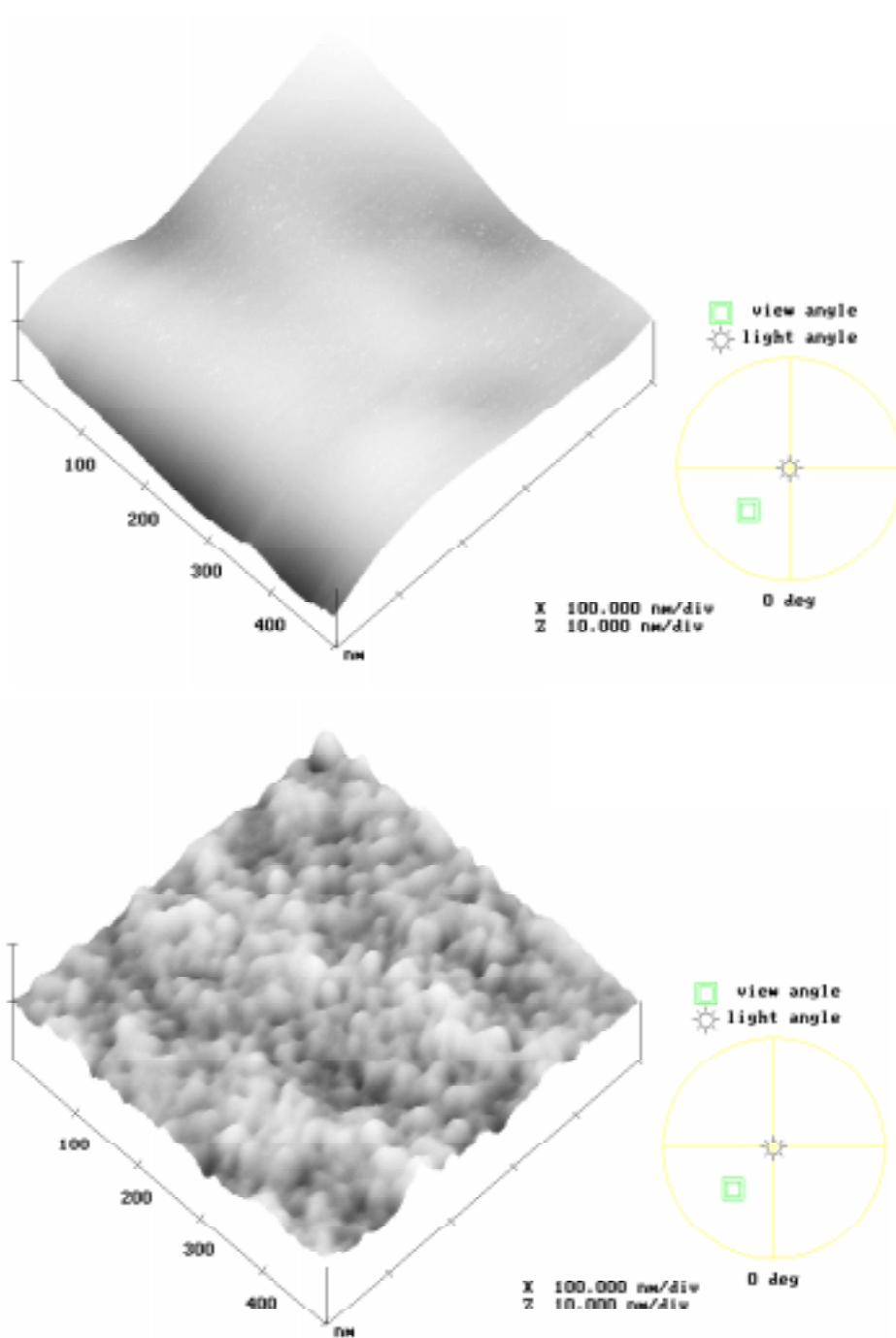
Figure 4:
Atomic force height image micrographs of an F-ester film (top) and an F-terminated segment film (bottom).
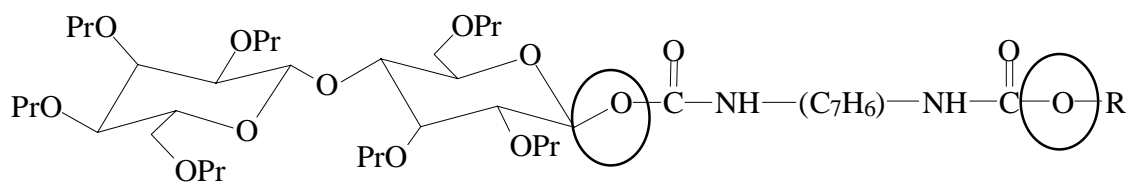
telechelic oligomer
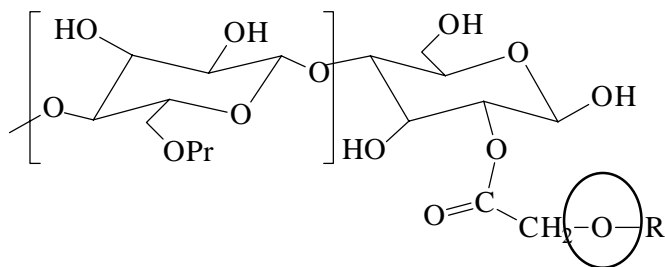
statistical copolymer

ether bond

R = CF3   (trifluoro)
  = CF2H   (difluoro, only statistical copolymer)
  = CF2CF2CF2CF2H   (octafluoro)
  = CH2CF2CF2CF2CF2CF2CF3   (perfluoro, only telechelic segment)

Figure 5:
Indication of ether bonds in terminated segments (top) and statistical F-esters (bottom)
which are believed to be involved in reorganization
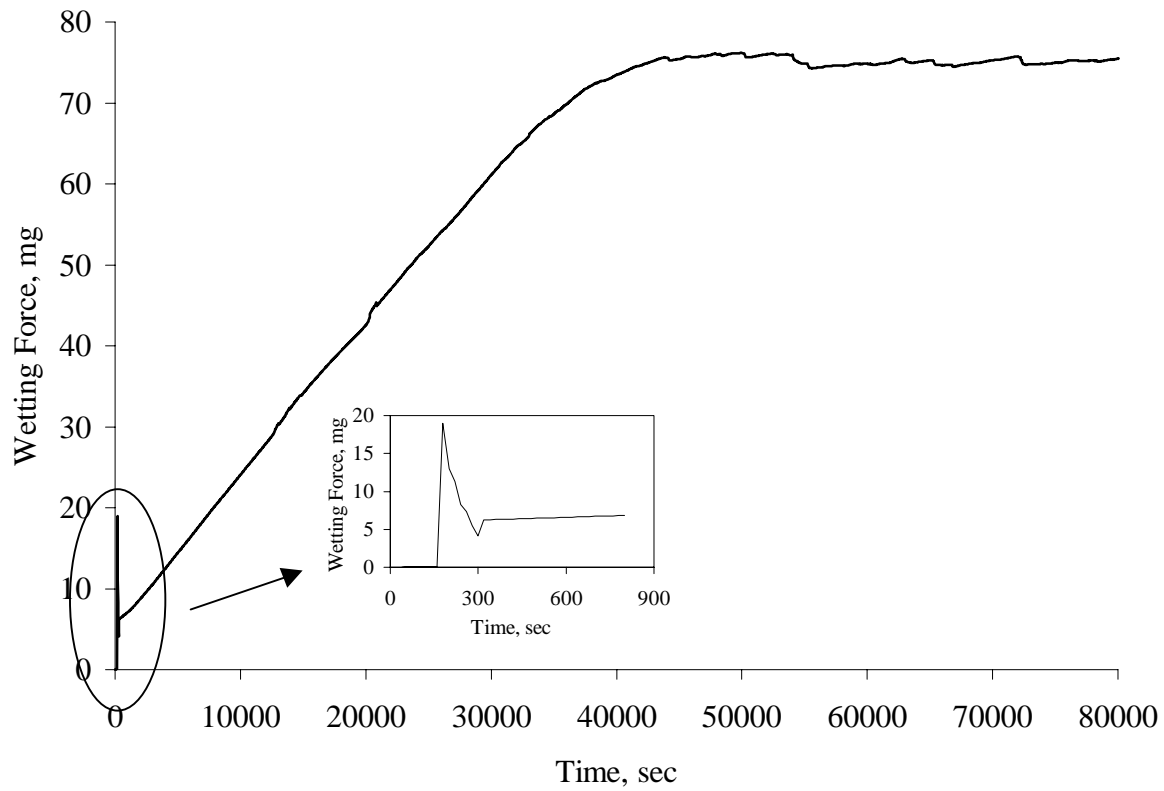
Figure 6:
Wetting force increase depending on time. The spike at the beginning of the experiment is due to the immersion of the sample into water. After a duration of linear increase, the force levels off. The phase of linear increase can be expressed by a linear equation. The equation is used to calculated weight gains of the films due to sorption (see text).
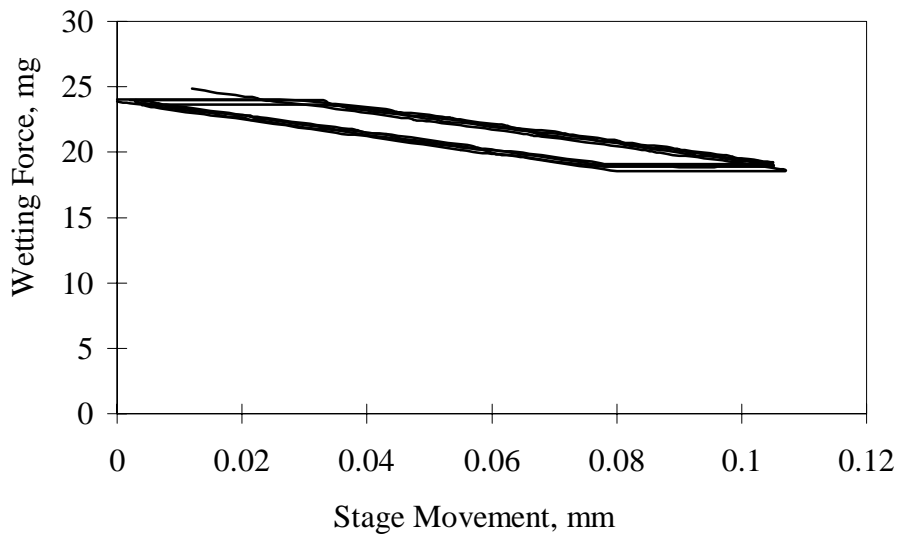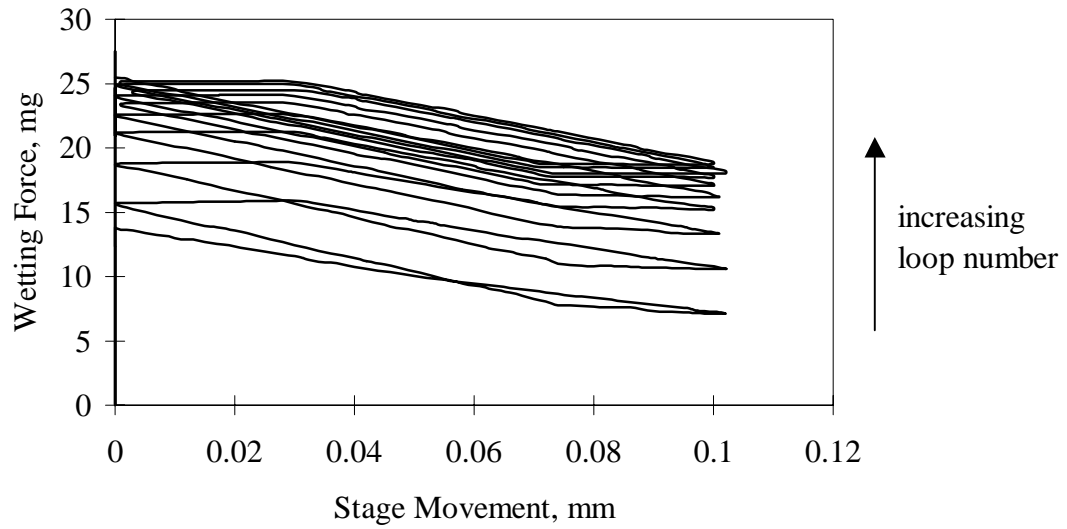
Figure 7:
Wetting force traces for consecutive loops. Typical behavior of F-containing films (top) and CP (bottom).
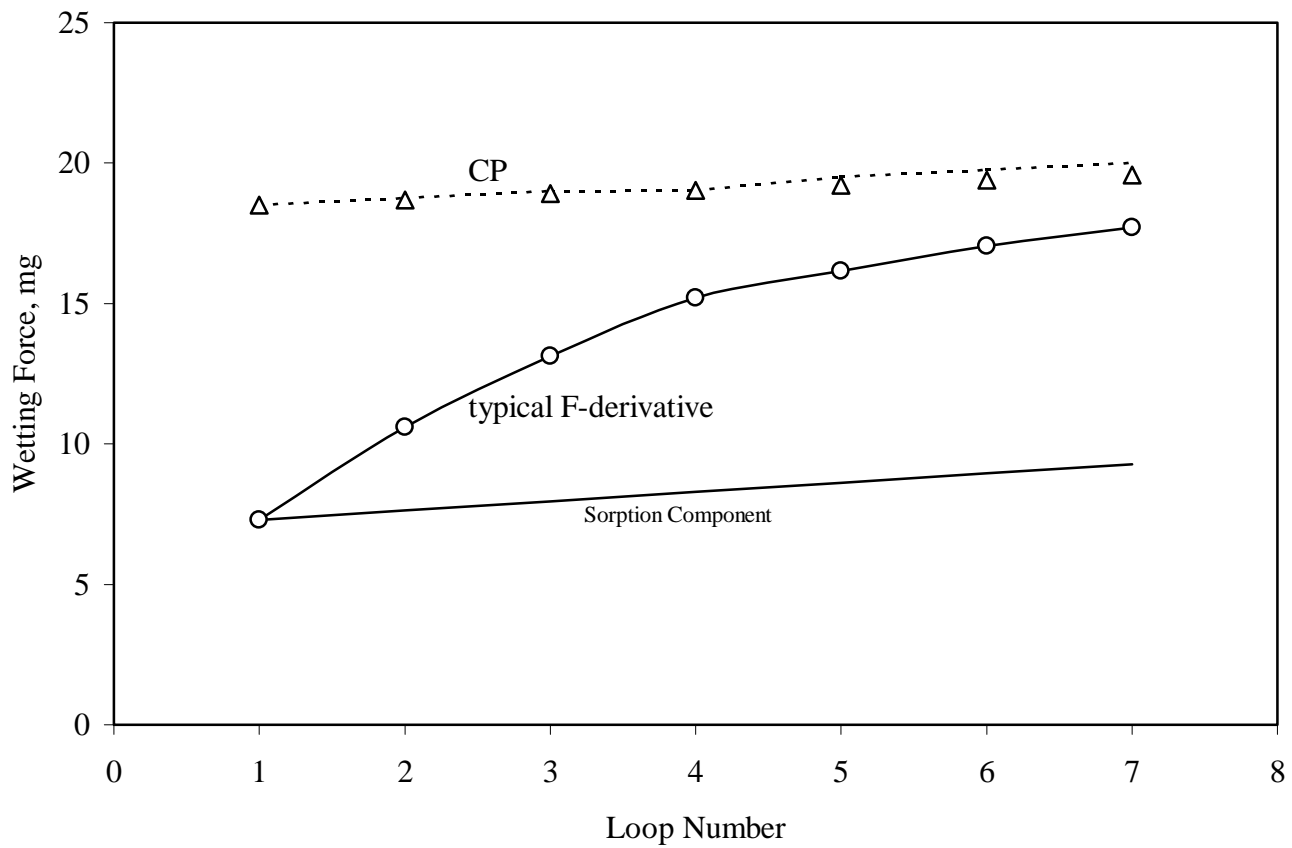
Figure 8:
Advancing wetting forces depending on loop number for CP and a typical F-derivative. The data for CP agree well with force values calculated using the slope value of the sorption experiment (-----), whereas in the case of the F-derivative the force increases more rapidly than according to the sorption data (——).
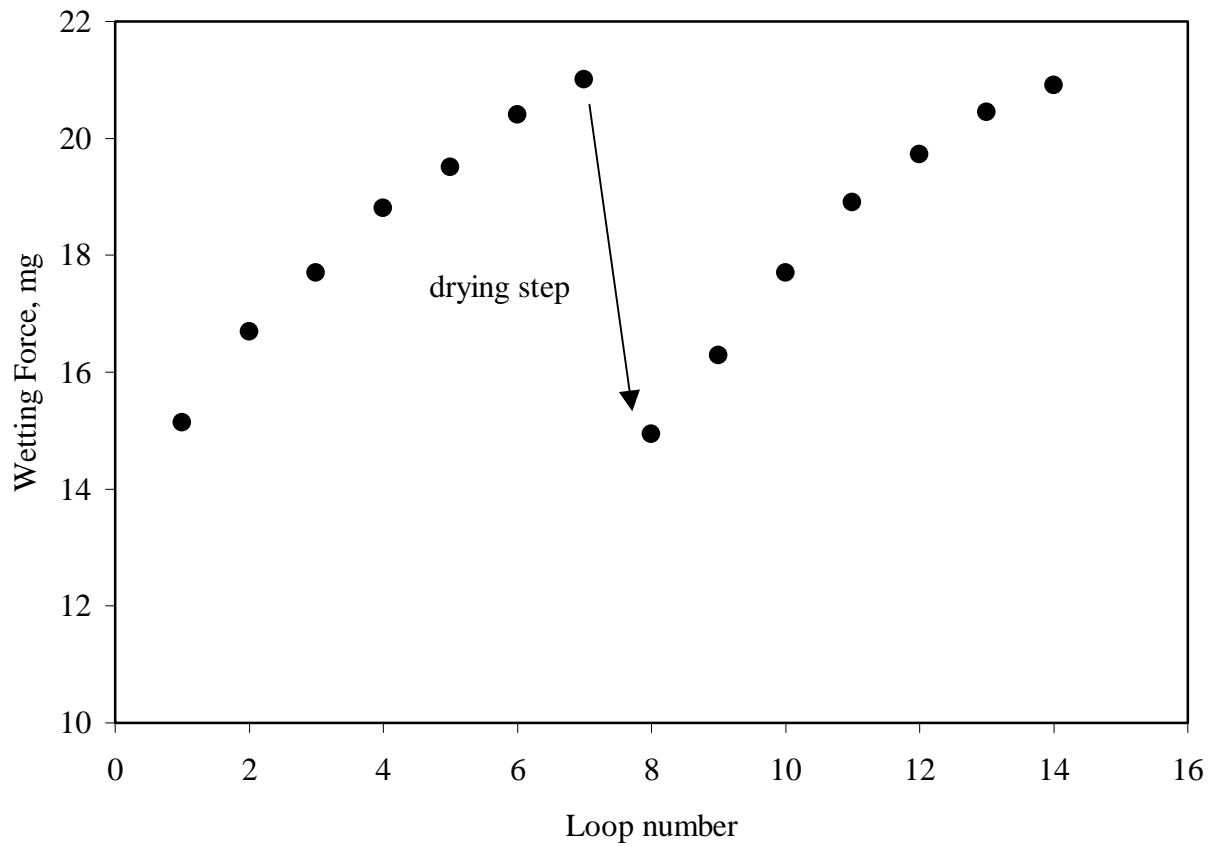
Figure 9:
Typical result for test of reversibility. In the initial experiment, the force increases with increasing loop number (as discussed in the text). After a drying step, the original wetting force is observed, indicating reversibility.