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Towards mapping of functional group distributions in functional polymers by AFM force titration measurements

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We report on the mapping of functional group distributions at flat, functionalised polymer surfaces with a sub-50 nm resolution by means of pH-dependent AFM force titration measurements using chemically modified tips.

The presence *and* spatial distribution of functional groups in polymer coatings or surface-treated bulk polymers play an important role in determining the interfacial properties of these materials.[1] While there are numerous techniques available which allow one to identify and analyse the functional groups introduced by, *e.g.* a surface modification reaction, the determination of the lateral spatial distribution of these functional groups, and the characterisation of their local environment on a sub-100 nm scale remains difficult to impossible with these techniques.[2,3]

As shown here for the first time, atomic force microscopy (AFM) with chemically functionalised tips was successfully applied to tackle this problem. The work described here combines the strategies of AFM tip modification[4] and *active* external control of tip–sample interactions in nanometer-scale AFM adhesion measurements on polymers which contain ionisable functional groups.[5–8] In particular, it is shown that pH-dependent force titration measurements allow one to map functional group distributions with a sub-50 nm resolution. The results obtained on three different polymer model systems, *i.e.* oxyfluorinated isotactic polypropylene (iPP),[9] plasma polymerised allylamine (PPAA),[10] and ammonia plasma modified polypropylene (PP), will be discussed.[11]

The interfacial properties of three different types of polymer surfaces were investigated in AFM force-distance measurements. The model surfaces differ in the type and local environment of the functional groups which are exposed at the free film surface. As shown in previous studies, PPAA contains amino groups,[10] oxyfluorinated iPP carboxylic acid groups,[12] and ammonia plasma modified PP basic (amino) groups.[11] The adhesion properties of these samples can be expected to differ strongly as a result of the different surface chemistry.

Gold-coated AFM tips were functionalised with ω-hydroxy-substituted thiols in order to adjust the interactions between tip and sample surface.[4,5,7–9,13] In an aqueous medium, hydroxy-terminated tips were previously shown to possess pH independent adhesion properties.[5] In these experiments the ionisation state of the exposed functional groups in the polymer films was varied systematically *in situ* by adjusting the pH of the aqueous medium while maintaining a constant ionic strength.[14]

Pull-off forces were evaluated from 100 force–distance curves for each pH.[15] Depending on the pH exclusively repulsive, both attractive and repulsive, or exclusively attractive interactions were detected.

The average pull-off force as a sum of attractive (van der Waals and dipolar) and repulsive (electrostatic) forces was calculated as peak maximum of a Gaussian distribution fitted to the corresponding histograms. The mean value found depended on the pH of the aqueous solution. As is shown in Fig. 1, the average pull-off forces exhibited a behaviour similar to conventional titration experiments. Force titration experiments have been performed previously by Lieber and coworkers[5] and van der Vegte and Hadziioannou,[7] without being accompanied by force volume imaging. For low pH values the PPAA and PP samples, which contain basic amino groups, showed negligible pull-off forces, while at pH >5 the adhesion was quite pronounced. An opposite trend was observed for the carboxylic acid-containing oxyfluorinated iPP, while the untreated iPP (without functional groups) showed no pH dependent pull-off forces.

The reduction of the pull-off forces as a result of repulsive interactions can be attributed to the presence of protonated amino groups for the PPAA and PP (low pH), and deprotonated

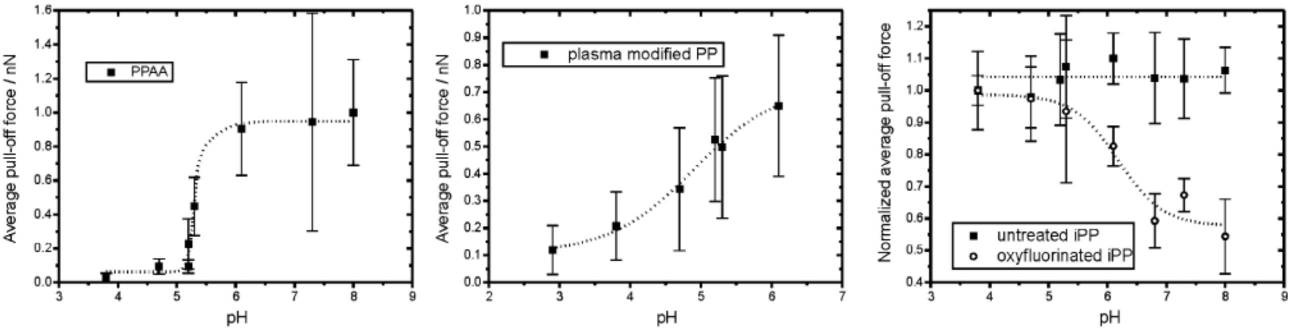

Fig. 1 Force titration data acquired with hydroxy-terminated tips for representative samples of the three model surfaces studied. For PPAA (left) and ammonia plasma modified PP (middle) the average pull-off forces are shown, for the untreated and oxyfluorinated iPP (right) the values were normalised to the values found for pH 3.8 (errors bars correspond to the standard deviation of the mean determined from the pull-off force distribution histograms). The dotted lines have been added to guide the eye.

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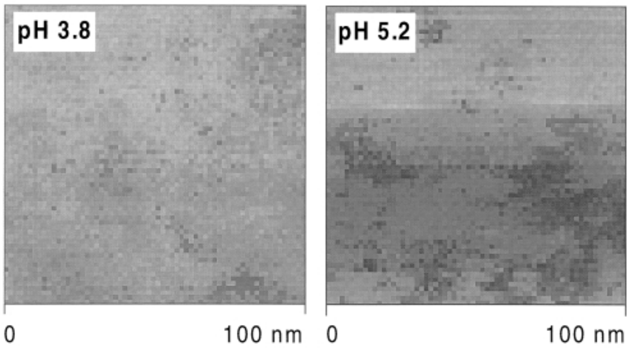

Fig. 2 Pull-off force images of a plasma polymerised allylamine film (peak power 175 W, duty cycle 10/10)[10] at different pH. In the force images dark regions indicates high adhesion (−0.1, −0.5 nN for pH 3.8 and 5.2, respectively), bright regions indicates low adhesion (*ca.* 0 and −0.1 nN for pH 3.8 and 5.2, respectively).

carboxylic acid groups in the iPP (high pH), respectively. The inflection points (force pK_a) are closely related to the thermodynamic surface pK_a values.[16] It is obvious that the force pK_a values are shifted relative to the known p*K*a values (in solution) for carboxylic acids and amino groups (acetic acid: pK_a 4.8; ethylamine: pK_a 10.7). The force pK_a values are shifted to a higher pH for the acidic groups, while for basic groups they are lower. Similar shifts were previously observed experimentally[5,17] and were related to the hydrophobicity of the local environment of the corresponding functional groups. This general interpretation is corroborated by recent simulations.[18] The more hydrophobic the local environment, the more difficult it becomes to create a charge due to the lower dielectric constant of the environment.

The shift of the force pK_a values observed in average force measurements can be used to differentiate between functional groups in different local environments. Depending on the hydrophobicity of the environment and on the local density of (electrostatically interacting) functional groups, these will either be ionised or neutral at pH values close to complete ionisation/neutrality. As indicated in the average adhesion measurements (*vide supra*) the adhesion properties are dramatically different for these two cases. Thus, by carefully adjusting the pH of the solution, areas where ionisation begins can be detected with a spatial resolution of 20 nm or better. This is shown in Fig. 2.

At pH 3.8 the amino groups of the PPAA are completely deprotonated which results in negligible adhesive forces. When the pH of the solution is adjusted to values close to the force pK_a, the spatial distribution of the pull-off forces is inhomogeneous. In the areas with pronounced adhesion the amino groups are neutral (dark patches in Fig. 2, right), while in the other areas repulsive or only weakly adhesive force are detected (bright areas in Fig. 2, right). The observed inhomogeneous distribution of amino groups at the surface of PPAA is most probably related to inhomogeneous temperature distribution in the plane of the film during the polymerization or different reaction pathways due to inhomogeneous initial coverage or *initially* deposited reaction products. This may lead to a heterogeneous restructuring of the polymer and the reorientation of the amino groups upon initial aging of the films in air similar to the processes observed previously.[19]

The data shown here constitute to our knowledge the first results on laterally resolved *imaging* of functional group distributions on polymers on a *sub*-50 nm level using scanning force microscopy with chemically modified tips (‘chemical force microscopy’). pH-dependent pull-off force measurements carried out on various functional polymers using OH-functionalised tips revealed laterally inhomogeneous pull-off forces. These inhomogeneous forces can be related to variations of local ‘pK_a’ values and different local hydrophobicity, and thus to inhomogeneous distribution of the polar functional groups present at the polymer surface.

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15 Triangular shaped silicon nitride cantilevers with silicon nitride tips (Digital Instruments (DI), Santa Barbara, CA, USA), which were coated with 2 nm Ti and 75 nm Au in high vacuum (Balzers), were functionalised with 11-hydroxyundecanol following the procedures described in refs. 8 and 9. The SFM measurements were carried out with a NanoScope III multimode SFM (DI) with modified tips in buffered aqueous solutions of constant ionic strength utilising a liquid cell (DI). The force distance curves used for construction of force titration curves were obtained with at least 10 different positions for each sample. For laterally resolved pull-off force measurements the AFM was operated in the force volume (FV, DI) mode. Only subsequent up and down scans which showed the same force characteristics were considered.

16 A strict quantitative evaluation, such as described by Hu and Bard (K. Hu and A. J. Bard, *Langmuir*, 1997, **13**, 5114), is at this point not possible due to uncertainties of the tip shape (granular gold coating) and the unknown effect of the morphology of the polymer films.

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