Surface Characterization of Oxyfluorinated Isotactic Polypropylene Films: Scanning Force Microscopy with Chemically Modified Probes and Contact Angle Measurements

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Received October 2, 1997; Revised Manuscript Received March 9, 1998

ABSTRACT: The surface of isotactic polypropylene (iPP) films modified by oxyfluorination was studied by a combination of complementary techniques to elucidate the effect of the modification on the chemical composition, surface energy, and morphology. The elemental composition was measured by X-ray photoelectron spectroscopy (XPS), and the surface free energy was characterized by contact angle measurements with different liquids. Following the approach by Good and co-workers, the acid−base characteristics of the modified polymer surfaces were estimated. Subsequently, the modified iPP films were investigated by scanning force microscopy (SFM). In tapping mode SFM, the sample topography was imaged and the surface roughness was quantitatively determined. Gold-covered SFM probes modified with carboxylic acid and methyl terminated self-assembled monolayers of thiols were used to determine the pull-off force distributions in ethanol. The interaction of the treated polymer film surfaces with chemically functionalized SFM tips was shown to correlate with the surface tensions obtained by contact angle measurements. In particular, pull-off forces measured with carboxylic acid functionalized tips in ethanol depended approximately linearly on the basic part of the surface free energy of the polymer film surface.

Introduction

Macromolecular materials with good bulk characteristics often possess poor surface properties. However, the surface properties of polymers have a profound influence on the final product application. For example, painting, metallizing, bonding, and printing require a good substrate adherence.[1] Thus apolar polymers such as polyolefins are usually surface-modified in order to introduce polar functional groups. The modification of polymer surfaces is therefore an area of tremendous scientific and commercial interest.

Surface modification of polymers can be accomplished by corona, flame, or plasma treatments or wet chemistry.[2] The resulting surface compositions can be measured with numerous techniques which provide average information on, e.g., functional groups created at a surface. Whitesides et al.[3,4] have demonstrated that a combined approach with contact angle measurements (wettability), X-ray photoelectron spectroscopy (XPS), and attenuated total reflection FTIR (ATR FTIR) provides detailed and defined ***in depth*** information on the composition of a treated polymer surface (of several angstroms for wettability, up to 10 nm for XPS, and about 1 μm for ATR FTIR).

The disadvantage of all these methods however, is their limited resolution ***laterally*** on the surface. For example, in conventional XPS the area analyzed at the sample surface has dimensions typically between 0.1 mm and few millimeters, whereas small area XPS used for photoelectron imaging is limited to a lateral resolution of 10 μm.[5] The lateral resolution is slightly better for ion microscope imaging with secondary ion mass spectroscopy (SIMS); the resolution in typical practical implementations is on the order of 100 nm.[6] Thus, it is not surprising that little is known about the lateral distribution of the functional groups generated by the surface treatment of polymers.

In general, scanning force microscopy (SFM) is an ideal tool for the study of surfaces in *both a micrometer and a nanometer size regimes*. The different imaging modes of SFM provide information about height and friction, modulus, stiffness, elasticity, magnetic and electrostatic forces, and more.[7] In particular soft organic surfaces such as polymers[8] or biological specimens can be characterized nondestructively. Also, the recently reported modification of SFM tips by a two-step process (covering the tip with gold and subsequent deposition of a self-assembled monolayer (SAM) of terminally functionalized thiols) has allowed several groups to quantitatively measure adhesion and friction forces between the functional groups exposed at the surface of the tip and films consisting of functionalized SAMs. By using this approach, chemically different areas on these defined model surfaces were distinguished due to differences in pull-off forces and friction ("chemical force microscopy").[9−13] The lateral resolution of SFM is usually at least 1 order of magnitude better than for the polymer surface characterization techniques mentioned above.

In our paper we present the first systematic study aiming at using chemical force microscopy to study polymer film surfaces with varying degrees of surface functionality. The ultimate goal of this study is to obtain new insights into the lateral distribution of functional groups with a resolution in the nanometer range. As a step in this direction, we present the results on a series of SFM measurements that successfully correlate the pull-off forces between chemically modified

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S0024-9297(97)01447-2 CCC: $15.00

SFM tips and the acid/base surface characteristics of oxyfluorinated[14−18] isotactic polypropylene (iPP) estimated by contact angle measurements.

The effect of surface treatments with fluorine containing gas mixtures on the wettability of polyolefines has been described previously.[14,15,19,20] The wettability was found to be largely influenced by the amount of oxygen present in the fluorine/nitrogen gas mixtures as well as the treatment time and process temperature. In addition, it was confirmed that the polymer surfaces became more hydrophilic after oxyfluorination.

The surface energy of oxyfluorinated polymers has been discussed by several authors.[14−18] The surface polarity determination was based on Wu's harmonic mean approach[15,18] and Zisman's critical surface tension approach.[16,17] Van Oss et al.[21] and Good et al.[22] showed that it is possible to treat the surface polarity phenomenon in terms of Lewis acidity and basicity (electron-accepting/proton-donating and electron-donating/proton-accepting functional groups, respectively).

In this work, the acid−base interaction theory was used to determine the surface free energy parameters γ_s^{LW} (Lifshitz−van der Waals interactions comprising dispersion, orientation and induction forces), γ_s^{+} (acidic term) and γ_s^{-} (basic term) of several oxyfluorinated iPP films. These parameters were related to the experimentally determined pull-off forces between chemically modified SFM tips and the treated iPP films.

Experimental Section

Sample Preparation. Isotactic polypropylene films (SOLVAY ELTEX P KL 177) were oxyfluorinated at 60 °C in a $F_2/N_2/O_2$ gas mixture. By variation of the treatment time and the gas composition, different surface compositions were achieved (see Results and Discussion for further details).

XPS. The XPS surface analysis was performed on a SSX 100 ESCA spectrometer (Surface Science Laboratories) at the University of Namur (Belgium). All spectra were taken at an electron take off angle of 35°.

Contact Angle Measurements. Contact angles were measured with water (Milli-Q), glycerol and diiodomethane on a contact angle microscope (G2, Krüss, Hamburg, Germany). The "recently advanced" technique described in ref 23 was employed with the syringe remaining in the drop at all times. The contact angles were measured on both sides of the drop and the results were averaged. The contact angles on oxyfluorinated polyolefin surfaces changed significantly over several weeks after the original oxyfluorination treatment. The chemical changes on the surface included hydrolysis of the acid fluoride groups to the corresponding acid groups or peroxy radical stabilization leading to the formation of oxygen containing groups.[24,25] Stable contact angles were measured ca. 5 weeks after the treatment. The surface free energy parameters were calculated according to ref 22.

Scanning Force Microscopy and Tip Modification. Triangular shaped silicon nitride cantilevers and silicon nitride tips (Digital Instruments (DI), Santa Barbara, CA) were covered with 50−70 nm of gold in a Balzers SCD 040 sputtering machine at an argon pressure of 0.1 mbar. The gold covered tips were then functionalized with 11-mercaptoundecanoic acid (−COOH) or octadecane thiol (−CH_3) following the procedures described in refs 26 and 27. The lattices of self-assembled monolayers of octadecane thiol or fluorinated thiols were imaged routinely with molecular (lattice) resolution on similar gold films deposited onto mica.[28]

The SFM measurements were carried out with a NanoScope III multimode SFM (DI). In this study, 1, 12, and 100 μm scanners were used. Tapping mode SFM scans were performed with untreated silicon cantilevers/tips in air (cantilever resonance frequency $f_0 = 280$−320 kHz). The force measurements were performed with unmodified silicon nitride tips and modified tips in ethanol (p.a., Merck) utilizing a liquid cell (DI). The force distance curves were obtained with at least five different positions from each sample, and the pull-off forces of single events were plotted in a histogram. The values of at least two independent tip−sample combinations were averaged.

Table 1. Surface Chemical Composition of Untreated and Oxyfluorinated iPP Films (XPS)

sample no.	% carbon	% fluorine	% oxygen
untreated	100		traces
1	59	27	14
5	77	4	19
150	57	24	19

Table 2. "Recently Advanced" Contact Angles θ_a (deg) of Untreated and Oxyfluorinated iPP Films

sample no.	θ_a water	θ_a glycerol	θ_a diiodomethane
untreated	99.8	87.5	63.3
1	74.9	66.4	62.9
5	66.0	61.2	61.0
150	51.1	56.4	57.9

Results and Discussion

The XPS analysis of the oxyfluorinated iPP films revealed that fluorine and oxygen atoms are present in the top 5−10 nm of the surface (for a discussion of surface−interface see refs 3 and 4). The XPS results are summarized in Table 1.

The surface treatment resulted in an increased hydrophilicity of the initial apolar polymer surfaces. The recently advanced contact angles measured with water, glycerol, and diiodomethane are listed in Table 2. A series of iPP films with increasing hydrophilicity was obtained by variations of the surface treatment parameters.

By using eqs 1−3, the surface free energy parameters were calculated according to ref 22. The parameters used to characterize surfaces include γ_s^{LW} (Lifshitz−van der Waals interactions comprising dispersion, orientation and induction forces), γ_s^{+} (acidic term) and γ_s^{-} (basic term).

$$\gamma_s^{LW} = \gamma_D(1 + \cos\theta_D)^2/4 \tag{1}$$

$$\gamma_G(1 + \cos\theta_G) - 2\sqrt{(\gamma_s^{LW}\gamma_G^{LW})} = 2\sqrt{(\gamma_s^{+}\gamma_G^{-})} + 2\sqrt{(\gamma_s^{-}\gamma_G^{+})} \tag{2}$$

$$\gamma_W(1 + \cos\theta_W) - 2\sqrt{(\gamma_s^{LW}\gamma_W^{LW})} = 2\sqrt{(\gamma_s^{+}\gamma_W^{-})} + 2\sqrt{(\gamma_s^{-}\gamma_W^{+})} \tag{3}$$

In eqs 1−3, θ denotes the measured recently advanced contact angles, and the subscripts D, G, and W denote diiodomethane, glycerol, and water, respectively. The combination of the acidic and basic terms yields the acid−base component of the surface free energy, γ_s^{AB}

$$\gamma_s^{AB} = 2\sqrt{(\gamma_s^{-}\gamma_s^{+})} \tag{4}$$

(eq 4). The total surface free energy γ can be calculated according to eq 5. The results of a numerical analysis

$$\gamma = \gamma_s^{LW} + \gamma_s^{AB} \tag{5}$$

using the experimental contact angle values are summarized in Table 3. The acid−base parameters of the

Table 3. Surface Energy Parameters of Test Liquids and Untreated and Oxyfluorinated iPP Films

sample	γ_s^{LW} (mN/m)	γ_s^{+} (mN/m)	γ_s^{-} (mN/m)	γ_s^{AB} (mN/m)	$\gamma = \gamma_s^{LW} + \gamma_s^{AB}$ (mN/m)
water	21.8	25.5	25.5	51.0	72.8
glycerol	34.0	3.92	57.4	30.0	64.0
diiodomethane	50.8	0	0	0	50.8
untreated	26.7	0.02	1.1	0.3	27.0
1	26.9	1.2	10.3	7.0	33.9
5	28.0	1.2	17.2	9.1	37.1
150	29.8	0.7	34.3	9.8	39.6

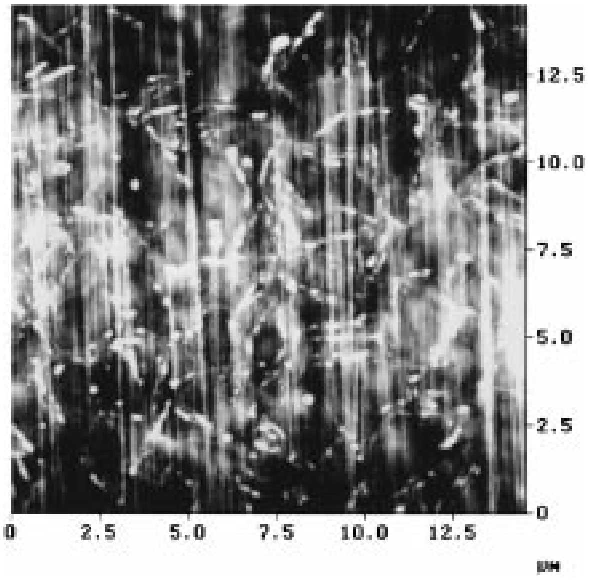

Figure 1. Untreated iPP film imaged with tapping mode SFM in air (z-scale 100 nm).

surface treated iPP films are listed together with the corresponding parameters of the test liquids used in the contact angle measurements.

As expected, the oxyfluorination process significantly increased the surface free energy (Table 3). It is interesting to note that the basic term γ_s^{-} is more informative about the surface changes introduced by oxyfluorination than the term γ_s^{AB}, which is influenced by the values of both the acidic and basic terms. By comparing the surface energy terms of samples no. 5 and no. 150, it becomes evident that although the value of γ_s^{AB} increases only slightly by 0.7 mN/m, the basic term γ_s^{-} shows an almost 2-fold increase.

The morphology of the iPP films was investigated by tapping mode SFM.[7] This resonating SFM technique allows one to significantly reduce shear forces between the tip and the surface during imaging, thus reducing sample deformation and damage. The tapping mode SFM images revealed some degree of etching on the surface due to chemical modification. A typical SFM height image of an untreated iPP film can be seen in Figure 1.

The machine direction of the untreated film (calendering) can be recognized as almost vertical stripes. In addition, filler particles were found to be located at the film-air interface. After oxyfluorination, the surface morphology still exhibited ridges due to the calendering process. However, the filler particles were partially removed and the roughness was increased. A typical tapping mode SFM micrograph of an oxyfluorinated film is represented in Figure 2.

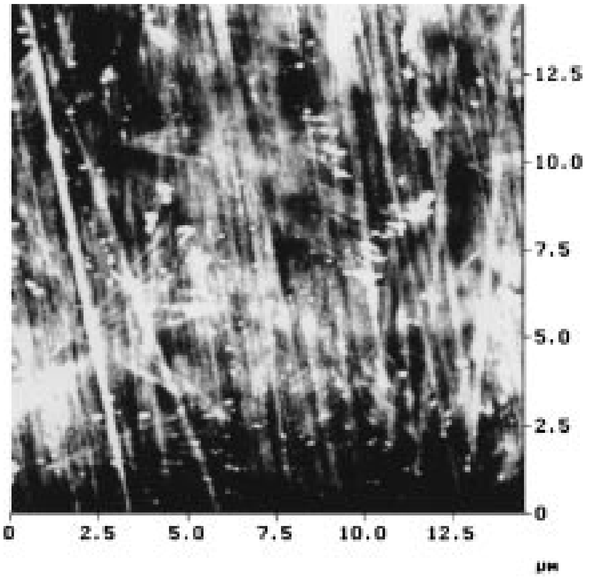

Figure 2. Tapping mode SFM image (height) of an oxyfluorinated iPP film obtained in air (sample no. 1) (z-scale 100 nm).

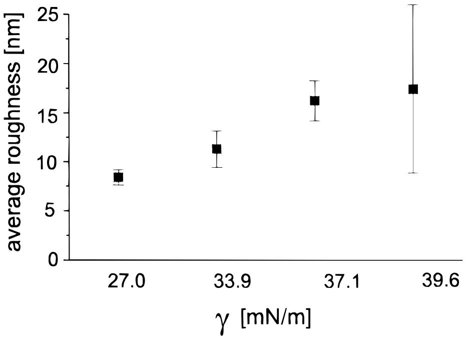

Figure 3. Average roughness R_A as a function of total surface free energy γ.

The mean roughness R_A for a surface is defined as the standard deviation of the height z with respect to the center plane z_{xy} within the scan area selected. The R_A values for all films were obtained by evaluation of (14 μm)^2 scans according to

$$R_A = \sqrt{\frac{\sum_{\substack{x=1,N\\ y=1,M}} (Z_{x,y} - \bar{Z}_{x,y})^2}{(N-1)(M-1)}} \qquad (6)$$

where N and M are the number of pixels in the x and y directions, and $Z_{x,y}$ is the image pixel height with respect to the center plane height $\bar{Z}_{x,y}$ for the pixel (x,y).

The R_A values calculated were averaged using at least five different images obtained at different locations on the sample surface. In Figure 3 the roughness data is plotted for films with different surface tensions. An increase of the standard deviation of the roughness data indicates a somewhat less uniform roughness distribution. The substrate roughness is of considerable importance for the evaluation of the force measurements presented below.[26] The pull-off force depends on the contact area between tip and sample. Therefore, the effect of *excessive* etching, which is concomitant with a

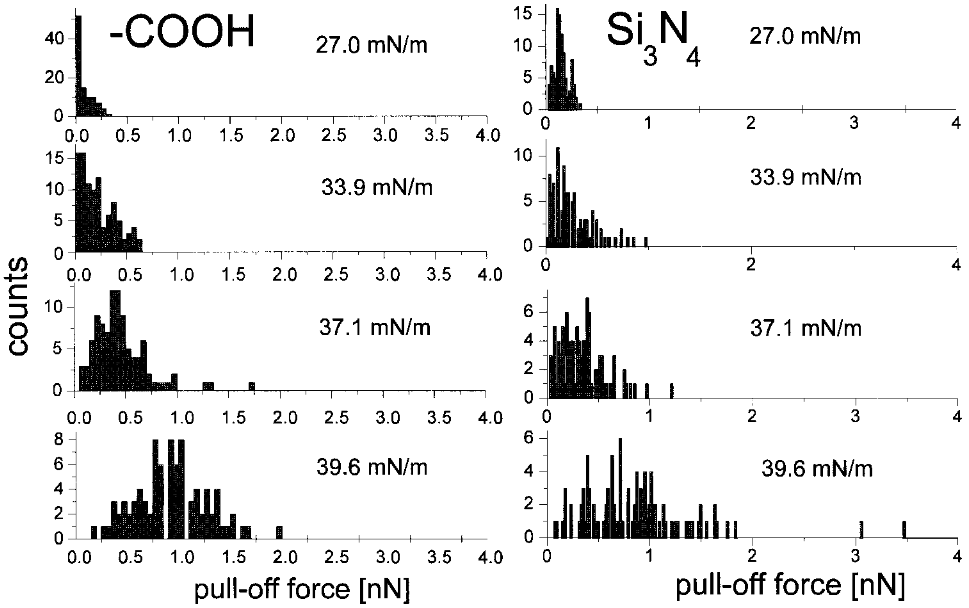

Figure 4. Histograms of pull-off force values obtained with a $-$COOH tip (left) and an unmodified Si_3N_4 tip (right) on untreated and oxyfluorinated iPP films in ethanol. The total surface free energy γ of the polymer film is shown.

significant increase in roughness, will mask specific interactions between the tip and the sample surface.

The variation in roughness for the films described in the present paper is much less pronounced as, e.g., in the gas phase fluorination of rubbers such as EPDM where the roughness increases from initially 30−50 nm to a final value of 300 nm after 1 h of treatment.[29] Thus, only a minor influence of the sample topology on the force measurements is expected.

As mentioned, the pull-off forces for different tip−sample combinations (all composed of highly oriented self-assembled monolayers of terminally functionalized thiols on gold) in ethanol were reported by Lieber et al.[9] In general, there is a trend that equal functional groups interact most strongly with each other. This trend can be understood on the basis of surface free energy considerations. The interaction between $-$COOH groups is, e.g., stronger than the mixed interaction between $-$COOH groups and $-CH_3$ groups. Methyl ($-CH_3$) groups have an intermediate pull-off force.

Recently, Sinniah et al.[13] complemented some of the observations of Lieber and co-workers by suggesting that for different solvent systems, such as water, solvent exclusion forces dominate the pull-off characteristics. We have evidence that in water solvent exclusion forces dominate the interaction between hydrophobic tips (methyl) and hydrophobic surfaces (such as poly(dimethylsiloxane), PDMS).[30] In ethanol however, the interactions observed in this and in an earlier study of our group[26] can be explained on the basis of Lieber's surface free energy arguments.

The results of the present study are summarized in Figures 4 and 5. All different polymer surfaces were probed with the *same* cantilever/tip assembly during one set of measurements, ensuring no variations in the radius of curvature of the tip. Variations in the contact area between consecutive force curve measurements are kept at a minimum, and the cantilever spring constant is unchanged.

The variations in the observed pull-off forces for the methyl group functionalized tip are much smaller than for the carboxylic acid functionalized tip. In Figure 5 the results obtained with a $-CH_3$ terminated tip were plotted only for the untreated film and the most hydrophilic film.

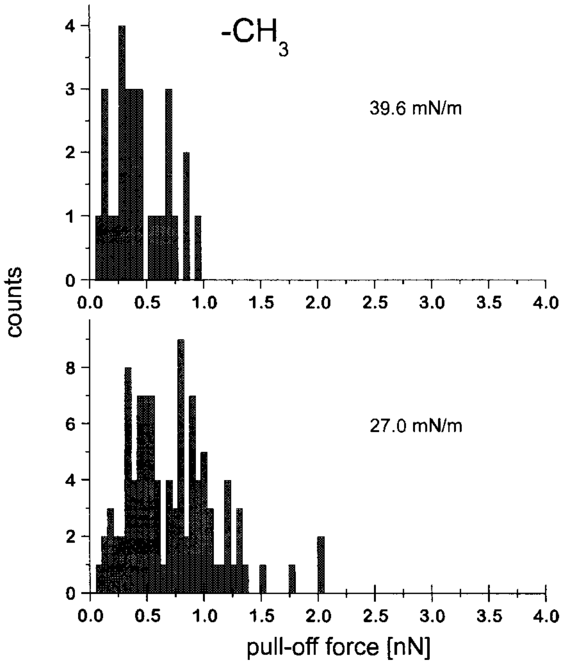

Figure 5. Histograms of pull-off force values obtained with a $-CH_3$ tip on untreated and oxyfluorinated iPP films in ethanol. The total surface free energy γ of the polymer film is shown.

In Table 4, the ratio of pull-off forces for a given film with respect to the film with the highest surface tension (sample no. 150) are summarized for tips with $-$COOH and $-CH_3$ functionalities. Note that by taking the ratios (normalized pull-off forces) the cantilever spring constant is canceled and the calibration of the spring constant (see e.g., ref 9) is therefore unnecessary. The ratios are stated along with the standard deviation obtained from different sets of measurements with different tips.

Measurements with unmodified (hydrophilic) Si_3N_4 tips have also been carried out in ethanol. The corre-

Table 4. Ratio of Pull-Off Forces of Film 150 and the Given Film Measured (a) with a −COOH Functionalized Tip and (b) with a $-CH_3$ Functionalized Tip

(a) −COOH Functionalized Tip

sample/γ (mN/m)	$F(x)/F$(39.6 mN/m)
27.0	0.16 ± 0.10
33.9	0.23 ± 0.01
37.1	0.47 ± 0.02
39.6	1.00

(b) $-CH_3$ Functionalized Tip

sample/γ (mN/m)	$F(x)/F$(39.6 mN/m)
27.0	1.57 ± 0.10
39.6	1.00

Table 5. Ratio of Pull-Off Forces of Film 150 and the Given Film Measured with a Si_3N_4 Tip

sample/γ (mN/m)	$F(x)/F$(39.6 mN/m)
27.0	0.18
33.9	0.30
37.1	0.40
39.6	1.00

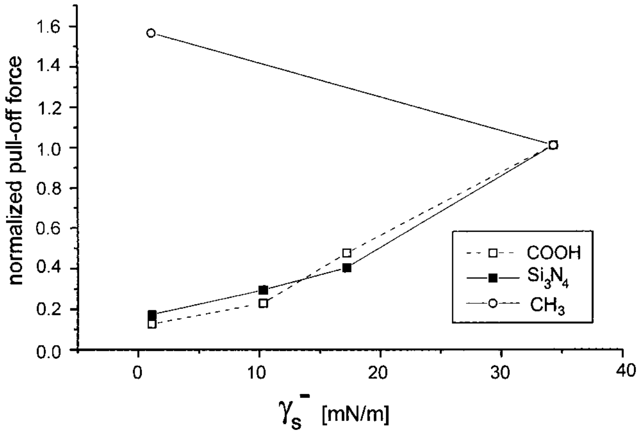

Figure 6. Normalized pull-off forces $[F(x)/F(150)]$ as a function of basic part of the surface free energy γ_s^-. For the guidance of the eye the data points have been connected by lines.

sponding normalized pull-off forces are given in Table 5. The "chemical specificity" is demonstrated by the ratio of the pull-off forces greater than 1.0 for the $-CH_3$ tip and less than 1.0 for the −COOH and the Si_3N_4 tips. In the first approximation, friction forces are proportional to the pull-off forces (or the adhesion) and the load, respectively, making these systems suitable to distinguish modified and unmodified areas on the polymer surface by performing additional friction force microscopy measurements.[9−11,12b,13]

The correlation between the contact angle measurements and the force measurements by SFM can be seen in Figures 6 and 7. As mentioned previously, the basic parameter γ_s^- of the surface free energy was found (by contact angle measurements) to be most sensitive for the changes of the surface chemistry and polarity. The average pull-off force between the (acidic) −COOH tip and the most basic polymer surface showed the highest value. Therefore, a plot of the normalized ratio of pull-off forces $[F(x)/F(150)]$ against the basic parameter γ_s^- of the surface free energy will be conclusive.

The ratio of pull-off forces for the −COOH modified tips was found to depend approximately linearly on the basic part of the surface free energy of the oxyfluorinated iPP surfaces. Qualitatively, the same result was obtained for the hydrophilic Si_3N_4 tip (Figure 6).[12] According to the interpretation of the wetting data, the Si_3N_4 tip can be considered acidic. The order of pull-off forces was reversed for hydrophobic $-CH_3$ tips which is indicative of "chemical contrast".[9]

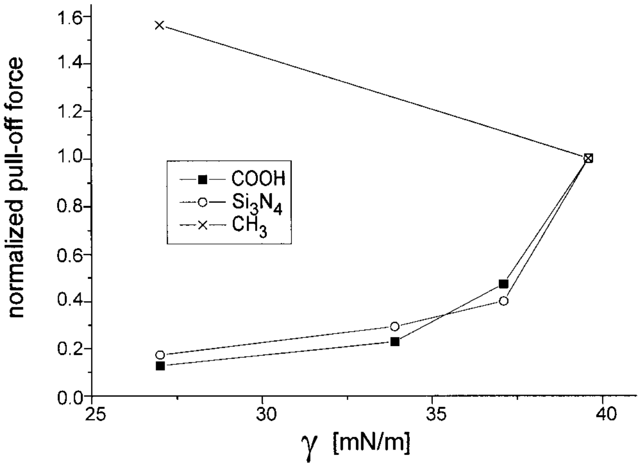

Figure 7. Normalized pull-off forces $[F(x)/F(150)]$ as a function of the total surface free energy γ. For the guidance of the eye the data points have been connected by lines.

In Figure 7, the normalized pull-off forces of the different tips used in this study are plotted as a function of the total surface free energy γ. The dependence is clearly nonlinear[31] and can be explained by considering the relation between the adhesion force and surface free energies. The adhesion force F_{ad} at pull-off predicted according to the JKR theory[32] depends linearly on the work of adhesion, W_{ST}

$$F_{ad} = -{}^{3}/{}_{2}\pi R W_{ST} \qquad (7)$$

where W_{ST} is the work of adhesion and R the radius of the tip. The work of adhesion is given as

$$W_{ST} = \gamma_S + \gamma_T - \gamma_{ST} \qquad (8)$$

where γ_S and γ_T are the surface free energies of the sample and the tip (in contact with ethanol) and γ_{ST} is the interfacial free energy of the two surfaces in contact. Unfortunately, the interfacial free energies γ_{ST} of the (treated) polymer surfaces and the functional groups on the tip are not known. Thus, it is not possible to determine both γ_S and γ_{ST} in a single experiment or to predict the dependence of the pull-off forces on the total surface free energy. We attribute the observed nonlinear relationship between adhesion force and total surface free energy to both the surface free energy of the polymer surface and the interfacial free energies.

The interaction between the tip and the polymer surface can be understood by taking into account the mechanisms of surface modification during oxyfluorination. The presence of oxygen during the fluorination of hydrocarbons leads to the formation of various oxygen functionalities such as carbonyl groups, α-fluorocarboxylic acids, peroxides, hydroxyl groups, ether groups (recombination of two radicals via an epoxy bridge), and acid fluoride groups that hydrolyze slowly in contact with atmospheric moisture to form carboxylic acids.[19,20,24] The hydroxyl, carboxyl, and carbonyl (enol form) groups that participate in hydrogen bonding increase the value of γ_s^+. The electron donor functionalities such as carbonyl (keto form), epoxy, ether, and ester groups influence strongly the value of γ_s^-. The hydrogen-bonding ability of fluorine is considered to be low,[16,17] so its influence on the surface acid/base behavior is probably not important. The interaction of this ensemble of functional groups with the highly ordered surface of the SAM at the apex of the SFM tip (or the unmodified Si_3N_4 tip) results in the observed pull-off forces. As mentioned above, the interaction between e.g −COOH groups is stronger than the mixed interaction between −COOH groups and $-CH_3$ groups, while methyl ($-CH_3$) groups have an intermediate pull-off force. The distributions observed can be attributed to variations in the contact area between tip and sample surface[26] as well as variations in the local distribution of functional groups.

The results presented here clearly prove that contact angle measurements that have a penetration depth of several angstroms,[3,4] and *average* pull-off force values by SFM using functionalized tips in a selected medium provide essentially similar information for polymers. Correlation of the results on oxyfluorinated iPP films can be done successfully by using the theory of surface acidity/basicity by Good and co-workers.[22] However, it should be noted that unlike wettability studies with contact angle microscopes, SFM possesses a high lateral resolution. In this current study, the question of lateral distribution of functional groups was not addressed. The limit of resolution in force measurements and chemical specific imaging is governed by the tip radius and has been estimated to be on the order of 10−20 nm.[9] In the first publications on chemical force microscopy it was anticipated that this technique could, in principle, be very valuable for the determination of functional group distributions on modified polymer surfaces.[9] To accomplish this important aim the technique will have to be further refined and improved. Difficulties in resolution will certainly arise due to variations in contact area between the generally rough topography of surface treated polymers (the modification is frequently a kind of etching process) and the SFM tip. However, we have recently demonstrated that molecular resolution imaging on uniaxially oriented fibrillar polymers remains possible with these modified tips.[27] Therefore, it is expected that the determination of functional group distributions on modified polymer surfaces will become possible to a certain extent soon.

Conclusion

The surface characteristics of a variety of oxyfluorinated isotactic polypropylene (iPP) films were investigated by XPS, contact angle measurements, tapping mode scanning force microscopy, and force measurements by SFM utilizing chemically modified probes. Following the acid−base surface free energy approach by Good and co-workers, it was found that the basic surface free energy term γ_s^- was most sensitive to the changes in surface chemistry and polarity. Tapping mode SFM revealed a rather small increase in surface roughness. Gold-covered SFM probes that were modified with carboxylic acid and methyl-terminated self-assembled monolayers of thiols were used to measure quantitatively the pull-off force distribution in ethanol. The interaction of the treated polymer film surfaces with chemically functionalized SFM tips was shown to correlate well with the surface tension parameters determined by contact angle measurements. In particular, pull-off forces measured with carboxylic acid functionalized tips in ethanol depended almost linearly on the basic surface free energy term γ_s^- of the polymer film surface.

Acknowledgment. The authors thank L. O'Connor for carefully reading the manuscript, and the Stichting Scheikundig Onderzoek in Nederland (Netherlands Foundation for Chemical Research) in the Priority Program Materials, the University of Twente, and Solvay S.A. (Belgium) for financial support.

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MA9714474