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Chemical Recognition of Antioxidants and UV-Light Stabilizers at the Surface of Polypropylene: Atomic Force Microscopy with Chemically Modified Tips

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We show in this paper that it is possible to locally detect additives on the surface of polypropylene with chemically modified atomic force microscopy (AFM) tips. Gold-coated AFM tips modified with methyl and hydroxyl terminated self-assembled alkanethiol monolayers were used to measure adhesion forces on a process-stabilizing agent (Irgafos 168), an antioxidant (Irganox 1010), and UV-light stabilizers (Tinuvin 770, Dastib 845, Chimassorb 944, and Hostavin N30). Pull-off force measurements carried out on these pure additive films have shown that it is possible to discriminate between antioxidants and UV-light stabilizers. We have evidenced a characteristic fingerprint for each additive, according to the functionality of the tip used and the medium wherein the force measurements are realized (water or nitrogen atmosphere). Similarly we have measured pull-off forces on a melt-pressed polypropylene sample stabilized with Irgafos 168, Irganox 1010, and Tinuvin 770. These adhesion force measurements show that the extreme surface of the polymer is mainly made of a layer of Tinuvin 770. These results have been compared to those obtained from time-of-flight secondary ion mass spectrometry measurements.

1. Introduction

The study of the reactivity and the chemical heterogeneity of material surfaces requires the development of surface chemical imaging tools allowing analysis of complex and multifunctional systems. Owing to their capacities to give original information on surfaces at the nanoscopic scale, scanning probe microscopies have an important role to play in this endeavor. A promising approach seems to be the combination of the unique lateral resolution of atomic force microscopies with designed chemical interactions between tip and sample.^{1–3} The deposition or grafting of active molecules on AFM tips enables measurements of interaction forces between chemical groups on the probe tip and molecules present on the analyzed surface. This is the principle of chemical force microscopy (CFM).

The ability of chemical force microscopy to image and discriminate areas exposing different functional groups on ultrathin films has no more to be proven. Interactions between chemically modified tips and various functional groups on the surface of self-assembled monolayers (SAMs) of alkanethiols have been extensively studied.^{4–7} These intermolecular force measurements have also been used in the case of biological materials to probe interactions

between ligands and receptors and antigen and antibodies, or between complementary DNA strands.^{8–11} Most of the CFM experiments described in the literature relate to model surfaces such as Langmuir–Blodgett films¹² or SAMs,^{4–7,13} but rarely on real complex systems. In the case of usual surfaces, such as polymers, numerous factors (roughness, morphologies, and mechanical properties, etc.) impede the correct interpretation of adhesion measurements. Schönherr and Vancso^{14–17} and some other groups^{18,19} have however succeeded in characterizing adhesion properties of polymer surfaces and, in particular, modified polypropylene surfaces, with chemical force microscopy.

In this context, this work aims at the development of chemical force microscopy techniques for chemical and molecular recognition at the surface of polymers. The properties of the topmost surface of polymeric materials are indeed crucial in many fields such as paint adhesion or biocompatibility.²⁰ These properties can be disrupted by the presence of additives on the surface. Indeed, to improve the stability and increase the lifetime of polymers,

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additives protecting them against thermal oxidation and UV-light are widely used. These additives are essential ingredients to ensure the stability of the material. UV-light stabilizers and antioxidants are usually present in the polymer matrix at a level of 1 wt % or less. But most of the additives have several disadvantages in applications and/or processing due to their propensity to migrate toward the polymer surface, causing blooming, adhesion failure, etc.²¹

In this paper, we present the results of a study on the ability of CFM to detect additives on polypropylene surfaces. Gold-coated AFM tips modified with self-assembled monolayers of ω -functionalized alkanethiols (octadecanethiol or 11-mercapto-1-undecanol) were used to measure adhesion forces. Before investigating polypropylene surfaces, it was necessary to determine the response of the additives toward the chemical probes. The investigated additives (Irgafos 168, Irganox 1010, Tinuvin 770, Dastib 845, Chimassorb 944, and Hostavin N30) are indeed large molecules containing several chemical functionalities, and it is quite difficult to anticipate which part or functional group of the molecule will determine the adhesive behavior.

In section 2, we describe the experimental details such as the procedure used for the preparation of the alkanethiol monolayers, and the conditions for the AFM data acquisition. In section 3, we undertake a systematic investigation of the adhesion forces between tips and pure additive films. Results obtained on a polypropylene sample containing three additives are also discussed. Finally, CFM results are compared to data obtained from time-of-flight secondary ion mass spectrometry (ToF-SIMS), which is a powerful technique for detecting additives on surfaces, as recently proved by Kersting et al.²² Concluding remarks are given in section 4.

2. Experimental Section

Materials. Gold substrates were prepared by evaporating titanium (50 Å) and gold (300 Å) onto silicon wafers (100) following the procedure described elsewhere.²³ The obtained substrates are polycrystalline with a (111) preferential orientation and a typical grain size of about 200–300 Å. Commercial Si₃N₄ tips (Microlever, ThermoMicroscopes, Sunnyvale, CA) were also coated with a 50 Å Ti adhesion layer and a 300 Å Au layer, following the same procedure. Octadecanethiol and 11-mercapto-1-undecanol (98%, Aldrich) have been used as received. Polypropylene and additives Irgafos 168, Irganox 1010, Tinuvin 770, Dastib 845, Chimassorb 944, and Hostavin N30 were received from Clariant Hünigues s.a. Irgafos 168 (phenol, 2,4-bis(1,1-dimethylethyl)-; phosphite (3:1)) is an antioxidant used as a process-stabilizing agent and Irganox 1010 (benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-2,2-bis[3-(3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)-1-oxopropoxy]methyl]-1,3-propanediyl ester) is an antioxidant. Tinuvin 770 (decanedioic acid, bis(2,2,6,6-tetramethyl-4-piperidinyl) ester), Dastib 845 (octadecanoic acid, 2,2,6,6-tetramethyl-4-piperidinyl ester), Chimassorb 944 (poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-

2,4-diyl][(2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl [(2,2,6,6-tetramethyl-4-piperidinyl)imino]], and Hostavin N30 (7-oxa-3,20-diazadispiro[5.1.11.2]heneicosan-21-one, 2,2,4,4-tetramethyl-20-(oxiranymethyl)-, homopolymer) are UV-light stabilizers belonging to the family of hindered amine light stabilizers (HALS). The additives are depicted in Chart 1. Water was deionized with a Millipore system to a resistivity of 18 MΩ cm. Ethanol (99.5%, Merck-Eurolab) and chloroform (99.8%, Merck-Eurolab) were used as received.

Sample Preparation. Prior to their use, the gold-coated tips and the gold substrates were cleaned to ensure a good adsorption of the thiols. They were freed from contaminants by UV/ozone treatment, and the treated substrates were then immersed in ethanol to remove the gold oxide before monolayer assembly.²⁴ Adsorption was then realized by immersing the gold substrates for 18 h in 10⁻³ M solutions of alkanethiols using absolute ethanol as a solvent. Upon removal from the solution, the samples were rinsed twice with *n*-hexane and absolute ethanol and gently dried in a nitrogen stream. The additive films were spin-coated from 10 g L⁻¹ chloroform solution onto silicon wafers. Polypropylene plates were obtained by compression molding on a mirror-polished stainless steel mold. The molding conditions were the following: polymer melting at 220 °C during 10 min, compression at 220 °C during 2 min under a pressure of 1.962 × 10⁷ Pa, and cooling under a pressure of 1.962 × 10⁷ Pa during 10 min.

Monolayers Quality. No atomic contamination could be found in the X-ray photoelectron spectra recorded from the thiol monolayers. The layers have also been characterized by contact angles measurements, ellipsometry, IRAS, HREELS, UPS, and photoemission with synchrotron radiation. Some of these results are described in ref 25.

ToF-SIMS Analysis. Positive and negative time-of-flight secondary ion mass spectrometry measurements were performed with a TFS-4000MMI (TRIFT) spectrometer from Phi Evans.²⁶ For spectrum acquisition, the sample was bombarded with pulsed primary ⁶⁹Ga⁺ ions (15 keV, 800 pA dc, pulse length < 1 ns when bunched (22 ns unbunched), and a repetition rate of 10.5 kHz). The analyzed area was either a square of 130 μm × 130 μm for the positive spectra or a square of 190 μm × 190 μm for the negative spectra. With a data acquisition time of 5 min, the total ion fluence was about 10¹² ions cm⁻², which ensured static conditions.²⁷ The secondary ions were accelerated to ±3 keV by applying a bias to the sample. The spreading of the initial energies of the secondary ions was compensated by deflection in three electrostatic analyzers. To increase the detection efficiency for high-mass ions, a postacceleration of 7 keV was applied at the entrance of the detector. Charge effects were compensated by means of a pulsed electron flood gun (*E_k* = 24 eV). Moreover, a stainless steel grid (nonmagnetic) with openings of 2 mm was put onto the sample surface in order to prevent variations of the surface potential. With these analytical conditions, the mass resolution (*m/Δm*) was about 3000 at *m/z* = 29. This is sufficient for the assignment of ions having the same nominal mass but different compositions, e.g. inorganic, hydrocarbons, oxygenated-containing fragments, etc.

AFM Measurements. AFM experiments were conducted with a PicoSPM equipped with a fluid cell and an environmental chamber (Molecular Imaging, Phoenix, AZ) and controlled by a Nanoscope III electronics (Digital Instruments, Santa Barbara, CA). We used silicon nitride cantilevers with a nominal spring constant of 0.1 N m⁻¹ and an integrated pyramidal tip whose nominal apex radius was typically equal to 50 nm (Microlever, ThermoMicroscopes, Sunnyvale, CA). All AFM measurements were performed in either nitrogen atmosphere or water rather than in air to eliminate or at least significantly reduce capillary forces. The adhesive interaction between tip and sample was determined from force vs cantilever displacement curves. In these

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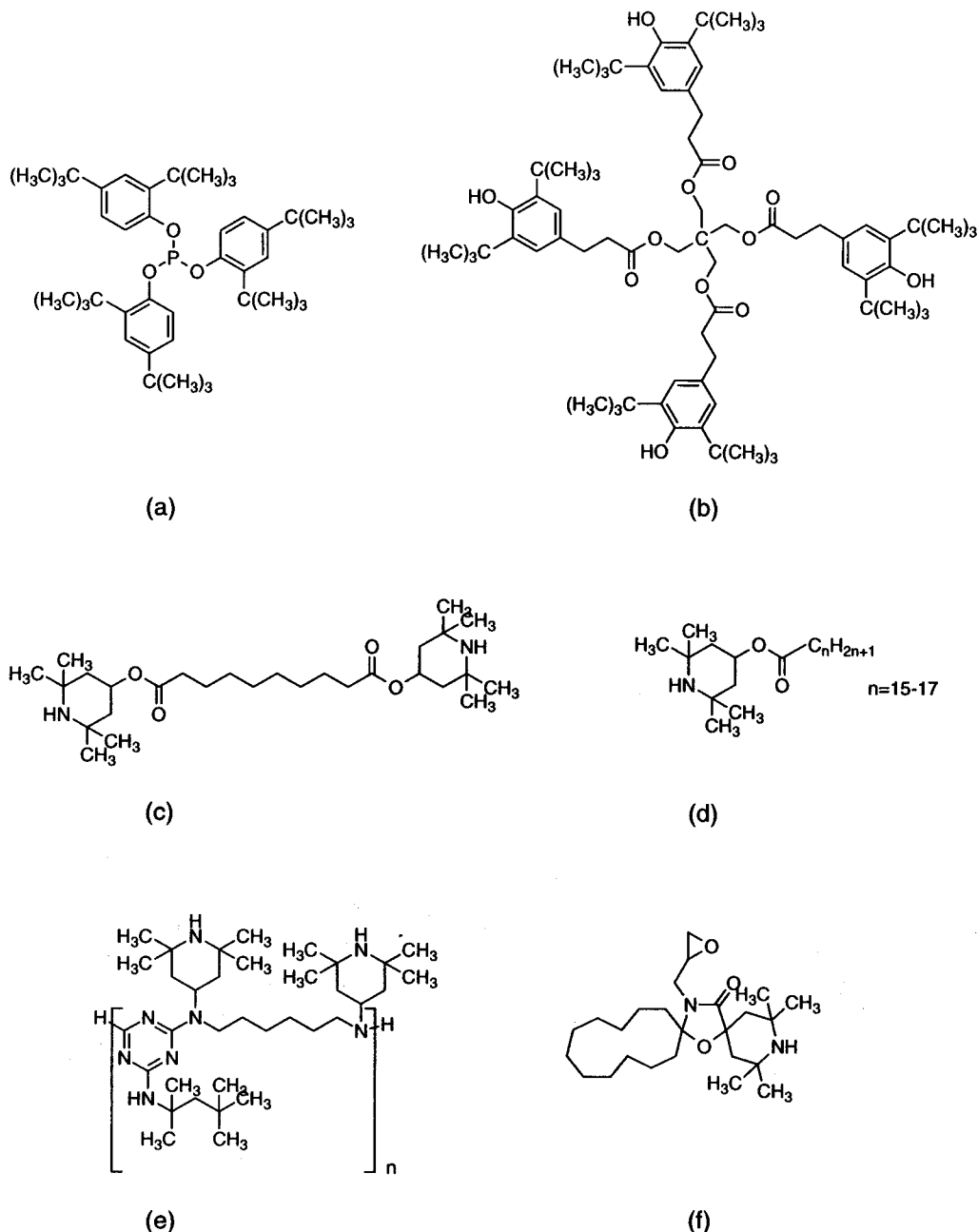
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Chart 1. Chemical Structure of Irgafos 168 (a), Irganox 1010 (b), Tinuvin 770 (c), Dastib 845 (d), Chimassorb 944 (e), and Hostavin N30 (f)

measurements the deflection of the cantilever is recorded as the probe tip approaches, contacts, and is then withdrawn from the sample. The observed cantilever deflection is converted into force using the nominal cantilever spring constant. Force-displacement curves were obtained using the "force volume imaging" mode. In this mode an array of force curves over the entire probed area can be obtained. A force curve is measured at each x - y position in the area, and force curves from an array of x - y points are combined into three-dimensional array of force data. Force volume enables the investigation of the spatial distribution of the interaction force between the tip and the surface. Using a program developed under Igor Pro (Wavemetrics, Portland, OR), the force volume data were treated in order to extract from every curve the pull-off force, or adhesion force, and to generate adhesion maps of the probed areas. To eliminate possible changes that could affect the measured pull-off forces, experiments were realized with two independent tips at three different locations for each sample. For every experiment, the average value of adhesion forces was determined from 1024 force-distance curves. The reported values of adhesion force correspond to the average

of the values measured for at least two independent tip-sample combinations.

3. Results and Discussion

The quality of the functionalized tips was checked by measuring the adhesive interaction on model surfaces. The average values of adhesion obtained in water, ethanol, hexane, and nitrogen atmosphere using tips and samples functionalized with SAMs terminating in either $-\text{CH}_3$ or $-\text{OH}$ groups are summarized in Table 1. The observed trend in adhesive force agrees with the expectation that interaction between hydrophobic groups ($-\text{CH}_3/-\text{CH}_3$) will be larger in water than in N_2 , whereas interaction between hydrophilic groups ($-\text{OH}/-\text{OH}$) will be smaller in water than in N_2 .²⁸ Adhesion forces values for $-\text{CH}_3/-\text{CH}_3$ and $-\text{OH}/-\text{OH}$ interactions depend also strongly on the solvent free energy.²⁹ The adhesion between $-\text{CH}_3$ moieties is strong in water (polar solvent) and very weak in

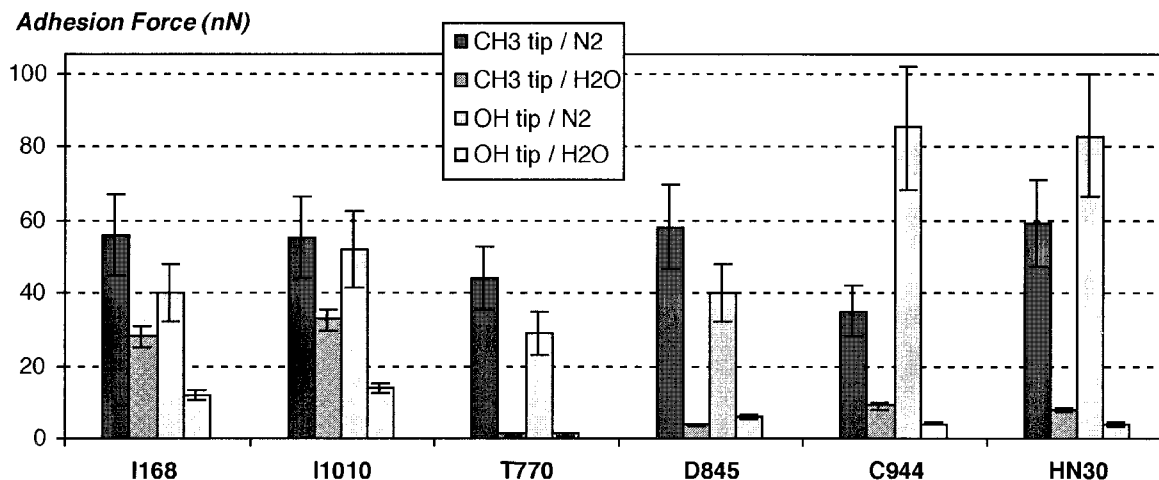


Figure 1. Average adhesion forces (nN) obtained with $-\text{CH}_3$ and $-\text{OH}$ terminated tips on Irgafos 168 (I168), Irganox 1010 (I1010), Tinuvin 770 (T770), Dastib 845 (D845), Chimassorb 944 (C944), and Hostavin N30 (HN30) spin-coated onto silicon wafers. The force-distance curves were recorded in water or in nitrogen atmosphere.

Table 1. Average Adhesion Forces Measured between Tips and Surfaces Functionalized with SAMs in Different Environments

medium	adhesion force (nN) tip/surface			
	$-\text{CH}_3/-\text{CH}_3$	$-\text{OH}/-\text{OH}$	$-\text{CH}_3/-\text{OH}$	$-\text{OH}/-\text{CH}_3$
water	46 ± 7	2.0 ± 0.3	6 ± 1	8.5 ± 1.3
hexane	0.1 ± 0.1	60 ± 12		
ethanol	0.9 ± 0.1	0.2 ± 0.1		
nitrogen	5 ± 1	180 ± 36	80 ± 16	60 ± 12

hexane (nonpolar solvent), whereas the adhesion between $-\text{OH}$ moieties is strong in hexane and weak in water. As expected, interaction forces obtained from $-\text{CH}_3$ tip and $-\text{OH}$ surface are similar to those obtained from $-\text{OH}$ tip and $-\text{CH}_3$ surface.

Adhesion force measurements between functionalized tips and surfaces were then used as routine operation in order to validate the grafting of functional groups on tips since common spectroscopic techniques are unable to characterize nanometer-sized tips. It is worth noting that the standard deviation is more important in N_2 (20–25%) than in water (10–15%), presumably due to capillary forces, which are not completely suppressed in N_2 .

Additive Films. Force-distance curves were recorded on additive films (process-stabilizing agent, antioxidizing agent, UV-light stabilizers) obtained by spin-coating onto silicon wafers. Average adhesion forces are reported in Figure 1. Since the purpose is to detect additives on the surface of polypropylene, it was necessary to establish a fingerprint for each additive in order to be able to recognize and to localize it on the polymer surface. Four sets of measurements have been carried out for each compound: pull-off forces have been recorded with $-\text{CH}_3$ and $-\text{OH}$ tips, in nitrogen atmosphere and in water. Each additive shows a characteristic fingerprint with respect to the tip functionality and the medium. The additives can be classified according to their adhesive behavior, which can be understood when considering their chemical structure. Irgafos 168 and Irganox 1010 have a very similar behavior. The fingerprint of Tinuvin 770 is similar to that of Dastib 845, and the fingerprint of Chimassorb 944 is similar to

that of Hostavin N30. Irgafos 168 and Irganox 1010 have a more hydrophobic behavior than the four other additives, as the adhesion obtained in water with a $-\text{CH}_3$ tip is rather high (typically about 30 nN). This behavior is probably due to the numerous *tert*-butyl groups present on these compounds. The ester moieties in Irganox 1010 are expected to be accessible to both electron donors and electron acceptors, but the hydrophobic interactions are obviously predominant. The *tert*-butyl groups are very bulky and probably mask the rest of the molecule. The surface is thus mainly composed of $-\text{CH}_3$ groups. Tinuvin 770 and Dastib 845 have a surfactant-like chemical structure. They are made of a hydrophobic alkyl chain and a hydrophilic head. They seem to behave like a hydrophobic system in nitrogen since the observed adhesion force for the $-\text{OH}$ tip is relatively small, compared to the adhesion force measured on the $-\text{OH}$ surface (Table 1). On the contrary, their behavior in water is typical of a hydrophilic system, with low adhesion forces for both $-\text{CH}_3$ and $-\text{OH}$ tips. They thus probably do not present the same conformation in nitrogen and in water. Hostavin N30 and Chimassorb 944 show an intermediate behavior. The methyl groups, especially on the Chimassorb 944 molecule, contribute to give rise to a hydrophobic behavior, whereas the amine groups give rise to a more hydrophilic behavior.

It is thus possible to recognize the additives from their fingerprint, or at least to recognize their family (antioxidants and UV-light stabilizers). Some of them cannot be distinguished such as Irgafos 168 and Irganox 1010 because of their very similar response toward the probes. It is worth noting that the adhesion force obtained with a $-\text{CH}_3$ tip in nitrogen atmosphere is not very usable as it is rather similar for all the additives. It appears in fact that one series of data (i.e. one type of chemical tip in one medium) is not sufficient by itself to identify an additive, but the whole combination of the four series is necessary.

Polymer Surfaces. The results obtained from adhesion force measurements carried out on polypropylene are presented in Figure 2. PPbs is a compression-molded polypropylene sample containing a basic stabilization: 0.05 wt % of Irganox 1010, 0.1 wt % of Irgafos 168, and 0.5 wt % of Tinuvin 770. A pure polypropylene surface is expected to behave like a $-\text{CH}_3$ terminated surface (Table 1 and Figure 2). The advanced contact angle of water on a polypropylene film is indeed around 100° .¹⁴ We should thus observe a high pull-off force when using a $-\text{CH}_3$

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Adhesion Force (nN)

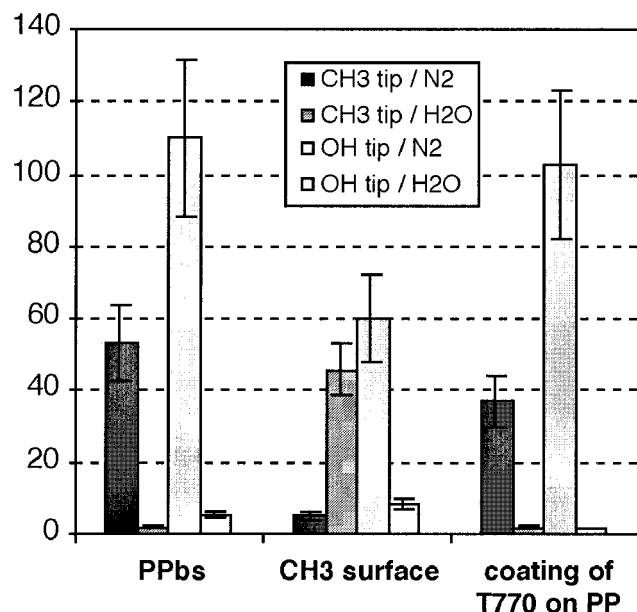


Figure 2. Average adhesion forces (nN) obtained with $-\text{CH}_3$ and $-\text{OH}$ terminated tips on stabilized polypropylene (0.05 wt % of Irganox 1010, 0.1 wt % of Irgafos 168, and 0.5 wt % of Tinuvin 770), on a $-\text{CH}_3$ terminated alkanethiol monolayer, and on a polypropylene surface on which a film of Tinuvin 770 has been spin-coated. The force–distance curves were recorded in water or in nitrogen atmosphere.

Table 2. Main ToF–SIMS Peaks (m/z) Observed in Pure Tinuvin 770, Irganox 1010, and Irgafos 168^a

Tinuvin 770		Irganox 1010		Irgafos 168	
+	–	+	–	+	–
58	340	57	231	57	63
124		203	277	147	79
140		219		219	205
212		259		441	457
342					473
481					

^a Ion structures can be found in ref 30.

terminated tip in water. On the contrary, we observe a rather small pull-off force (2 nN), i.e., 1 order of magnitude smaller than expected. Moreover, the adhesion observed when using an $-\text{OH}$ terminated tip is unexpectedly very high in N_2 and unexpectedly low in water. This adhesive behavior in water is similar to the one observed on oxifluorinated or on UV–ozone treated polypropylene films, and is typical of a rather hydrophilic polypropylene surface.^{16,18} The only compound present in the sample that could give rise to such a behavior is Tinuvin 770. Irganox 1010 and Irgafos 168 are much more hydrophobic (see Figure 1). The surface of PPbs is thus probably composed of a layer of Tinuvin 770. As a comparison, we have measured the pull-off forces on a pure polypropylene surface on which a film of Tinuvin 770 was spin-coated. The behavior of this surface (Figure 2) is very similar to the one observed for the PPbs surface, supporting the presence of Tinuvin 770 on the stabilized polypropylene sample.

The presence of Tinuvin 770 on the PPbs surface has been confirmed by ToF–SIMS measurements. The negative and positive mass spectra are shown in Figure 3a,b, respectively. The main positive and negative ToF–SIMS peaks for Irgafos 168, Irganox 1010, and Tinuvin 770 additives are collected in Table 2. The corresponding

structures can be found in ref 30. The peak at $m/z = 340$ (in the negative ToF–SIMS spectrum, Figure 3a) and at $m/z = 124, 140, 212, 254, 342$, and 481 (in the positive spectrum, Figure 3b) are characteristic fragments of Tinuvin 770. But peaks corresponding to fragments belonging to other compounds also appear in the spectra. The peaks at $m/z = 25, 49$, and 51 (Figure 3a) and at $m/z = 27, 41, 55$, and 69 (Figure 3b) are characteristic fragments of polypropylene. The peak at $m/z = 219$ (Figure 3b) is characteristic of Irganox 1010. The peaks at $m/z = 63, 79, 205, 457$, and 473 (Figure 3a) correspond to fragments from Irgafos 168. The three additives, initially contained in the bulk of the polymer, are thus present on the surface after material processing. However, CFM data (Figure 2) seem to indicate that only the hydrophilic additive is detected at the outermost surface.

The results obtained from both techniques can be correlated by the analysis of the adhesion map ($10 \times 10 \mu\text{m}$) obtained with a $-\text{CH}_3$ tip in water (Figure 4). This image, recorded at a resolution of 32×32 pixels (measurements were thus taken at about $0.3 \mu\text{m}$ intervals), shows the lateral distribution of pull-off forces. The great majority of pull-off forces correspond to low adhesion forces, around 1 nN (bright color). This is close to the typical adhesion force measured on Tinuvin 770 (2 nN). Arrows indicate small areas presenting high pull-off forces (10–20 nN). They can correspond to areas where polypropylene or the other additives (Irgafos 168 and/or Irganox 1010) are apparent. The diameter of these areas varies between 300 nm and $1.5 \mu\text{m}$. The major part of the surface area is thus covered by an external layer of Tinuvin 770. The average adhesion force measured by CFM thus corresponds to the adhesion force obtained on pure Tinuvin 770. On the contrary, ToF–SIMS measurements, which are not yet quantitative, show that the three additives are present on the surface. These adhesion heterogeneities could also be due to variations in surface roughness. Since the polypropylene samples are obtained by compression molding on a mirror-polished stainless steel mold, the roughness is rather low. Surface roughness profiles have been measured and the typical root mean square roughness is about 3 nm on $10 \times 10 \mu\text{m}$ images. The observed variations in pull-off forces do not correspond to topographical heterogeneities. There is no correlation between the areas of high adhesion and topographical defects.

4. Concluding Remarks

Chemical AFM probes, obtained by grafting of $-\text{CH}_3$ or $-\text{OH}$ terminated alkanethiol monolayers were used to record force–distance curves on additive films. Four sets of measurements were carried out for each additive: pull-off forces have been recorded with $-\text{CH}_3$ and $-\text{OH}$ terminated tips, in nitrogen atmosphere and in water. We have evidenced a characteristic fingerprint for each additive with respect to the tip functionality and the measurement environment. This fingerprint enables the differentiation of the additives. Antioxidants have a very different behavior from the UV-light stabilizers; they are much more hydrophobic. The results obtained on stabilized polypropylene (0.05 wt % of Irganox 1010, 0.1 wt % of Irgafos 168, and 0.5 wt % of Tinuvin 770) have shown that the extreme surface of the material is mainly composed of UV-light stabilizer (Tinuvin 770). The presence of this additive drastically influences the adhesion properties of the polymer. CFM adhesion mapping has been shown to

(30) Vickerman, J. C.; Briggs, D.; Henderson, A. *The Static SIMS Library—Part 2 Organic materials*; Surface Spectra: Manchester, U.K., 1999.

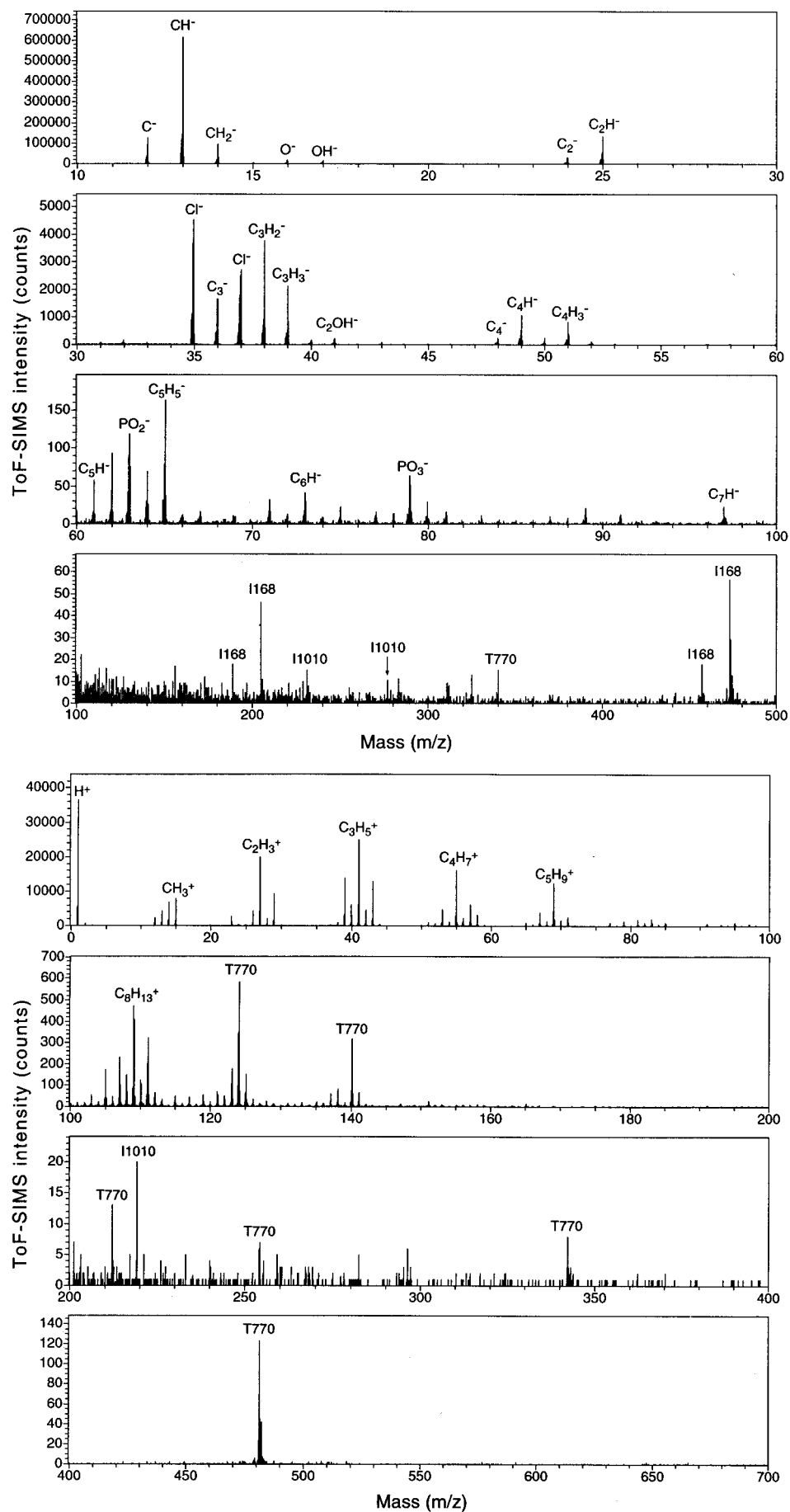


Figure 3. Negative (a, top) and positive (b, bottom) ToF-SIMS spectra of stabilized polypropylene (0.05 wt % of Irganox 1010, 0.1 wt % of Irgafos 168, and 0.5 wt % of Tinuvin 770).

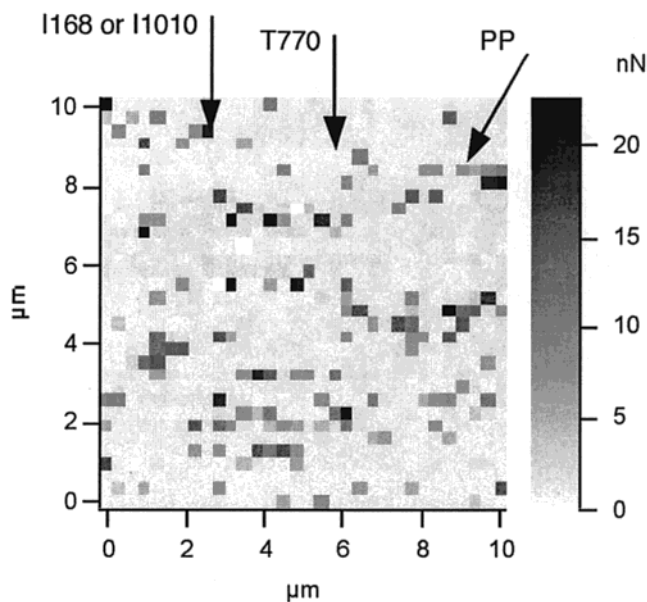


Figure 4. Adhesion map obtained on stabilized polypropylene (0.05 wt % of Irganox 1010, 0.1 wt % of Irgafos 168, and 0.5 wt % of Tinuvin 770) with a $-\text{CH}_3$ terminated tip in water. Dark shadings indicate high adhesion (10–20 nN), and bright shadings indicate low adhesion (1–2 nN).

be suitable to probe the chemical and adhesion heterogeneity at the surface of stabilized polypropylene. It allows

us to supplement the information that can be obtained by ToF–SIMS analysis. Indeed, ToF–SIMS data only give information about the presence of additives at the surface, and ToF–SIMS chemical imaging of additive distribution does not provide yet a submicroscopic lateral resolution.

The final aim of this investigation is to characterize adhesion and aging properties of polymers in correlation to the study of additive migration toward the material surface. As reported in this paper, laterally resolved chemical force microscopy enables one to study the distribution of chemical functional groups on the surface. These results constitute a significant step toward the ultimate aim of high-resolution chemical and molecular recognition at the surface of polymer films.

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