

# Mapping Aging Effects on Polymer Surfaces: Specific Detection of Additives by Chemical Force Microscopy

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We report in this contribution the successful application of chemical force microscopy to study aging of polymer surfaces at the submicroscopic scale. Adhesion force mapping using tips modified with methyl- and hydroxyl-terminated alkanethiols was used to probe the chemical composition of polypropylene surfaces as a function of aging time. We have measured adhesion force distributions on polypropylene melt-pressed films stabilized with antioxidants, process-stabilizing agents, and UV-light stabilizers. These adhesion force distributions were correlated with the additive distribution at the surface. We were able to evidence modifications of the local adhesion properties on the polymer surface due to material aging. These results support the conclusion that the UV-light stabilizer migrates toward the surface and forms a film that makes the surface less hydrophobic. Laterally resolved adhesion force maps show chemically heterogeneous surfaces on a sub-100 nm scale.

## 1. Introduction

The properties of polymeric materials (such as biocompatibility or adhesion) that control interfacial fracture, painting, metallizing, friction, and boundary lubrication are governed by the chemical structure of the topmost surface. Understanding the structure and dynamics of polymer surfaces is thus a challenge in numerous areas of tremendous scientific and commercial interest. Properties of polymer surfaces can be disrupted due to material aging. To improve the stability and increase the lifetime of polymers, additives protecting them against thermal oxidation and UV light are widely used.<sup>1–4</sup> Stabilization against thermal oxidation is essential for all organic polymers, since they are inevitably exposed to oxygen during synthesis, processing, storage, and use. Even relatively stable polymers undergo significant deterioration on long-term aging at ordinary temperature in air. The UV component of sunlight, in the 290–400 nm wavelength range, induces for example photochemical reactions.<sup>5</sup> This degradation can give rise to modification of mechanical and/or optical properties (surface aspect, transparency, decoloration, ...). Polypropylene and many other polymers are essentially useless until stabilizers are added. The weak tertiary carbon–hydrogen bonds in polypropylene makes it particularly susceptible to degradation caused by heat, oxidation, process shearing, and UV radiation. Additives are thus essential ingredients to ensure the stability of this 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, local adhesion failure, ....<sup>2–4</sup>

Moreover, with the development of miniaturization and nanotechnologies, the study of the reactivity and the chemical heterogeneity, but also the aging, of polymer surfaces requires the development of surface chemical imaging tools allowing the analysis of complex and multifunctional systems at the nanoscopic scale. The spatial arrangement of functional groups on material surfaces is crucial in numerous applications. Thoroughly controlled fabrication of highly defined ultrathin polymer films is of increasing importance in technical fields such as microelectronics and sensors. XPS and ToF–SIMS are powerful tools for the characterization of the chemical composition of polymer surfaces, but the disadvantage of these techniques is their laterally limited resolution, especially on polymer surfaces because of charging effects. Owing to their capacity 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 is the combination of the unique lateral resolution of atomic force microscopies with designed chemical tips.<sup>6,7</sup> The deposition or the grafting of active molecules on AFM tips enables the measurement 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).

Most of the CFM experiments described in the literature relate to model surfaces but rarely on real complex systems. Interactions between chemically modified tips and various functional groups on the surface of self-assembled alkanethiol monolayers<sup>6–12</sup> or Langmuir–

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Blodgett films<sup>13</sup> have been extensively studied. In the case of usual surfaces, such as polymers, numerous factors (roughness, morphologies, mechanical properties, ...) impede the correct interpretation of adhesion measurements. Some research groups have however succeeded in characterizing adhesion properties of surface-treated polymers with chemical AFM probes.<sup>14–20</sup> It is now important to assess the applicability of CFM to complex polymer systems. We have shown very recently that it was possible to detect the presence of additives at the surface of polypropylene by CFM.<sup>21</sup>

In this context, this paper is concerned with the study of polypropylene aging due to additive surface migration with a lateral resolution lower than 1  $\mu\text{m}$ . Gold-coated AFM tips modified with self-assembled monolayers (SAMs) of  $\omega$ -functionalized alkanethiols were used to measure local adhesion forces on pure and stabilized polypropylene and to compare the effects of aging on these materials. Adhesion maps were used to investigate the distribution of additives at the surface and the modification of this distribution due to polymer aging. The final aim of this investigation is to increase our knowledge of phenomena taking place in surface modifications induced by material aging.

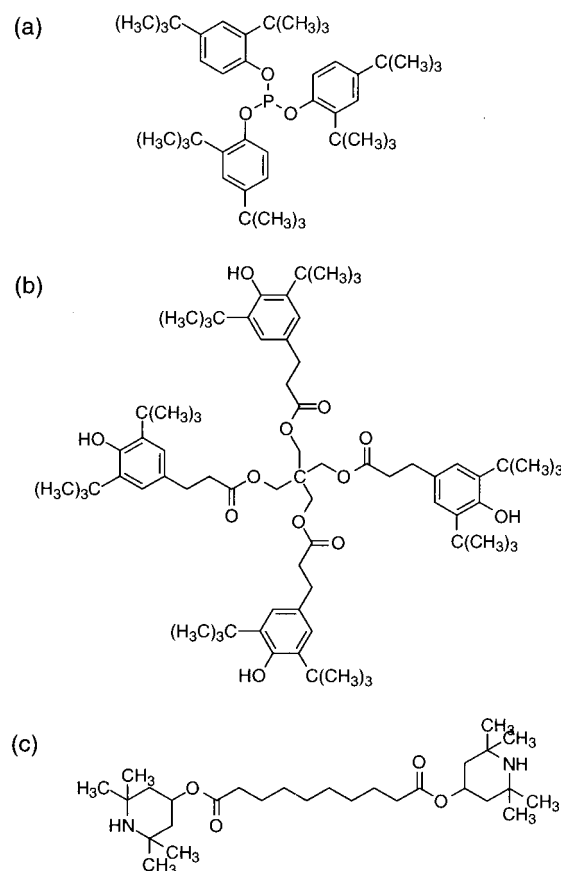
In section 2, we describe experimental details such as the procedure used for the preparation of the alkanethiol-modified probes and the samples, as well as the conditions in which the AFM data have been obtained. In section 3, we undertake a systematic investigation of adhesion forces between tips functionalized with octadecanethiol or 11-mercapto-1-undecanol and polypropylene surfaces. Concluding remarks are given in section 4.

## 2. Experimental Section

**Materials.** Gold-coated commercial  $\text{Si}_3\text{N}_4$  tips (Microlever, ThermoMicroscopes, Sunnyvale, CA) were prepared by evaporating titanium (50 Å) and gold (300 Å) following the procedure described elsewhere.<sup>22</sup> Octadecanethiol and 11-mercapto-1-undecanol (98%, Aldrich) were used as received. Polypropylene and additives (Irgafos 168, Irganox 1010, and Tinuvin 770) were received from Clariant Huningue sa. Irgafos 168 (2,4-bis(1,1-dimethylethyl)phenol 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) is a UV-light stabilizer 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 M $\Omega$  cm. Ethanol (99.5%, Merck-Eurolab), chloroform (99.8%, Merck-Eurolab), and dichloromethane (99.8%, Merck-Eurolab) were used as received.

**Tips and Sample Preparation.** The chemical grafting on the tips was realized following the procedure described in ref 21. Polypropylene plates were obtained by compression molding on

**Chart 1. Chemical Structures of Irgafos 168 (a), Irganox 1010 (b), and Tinuvin 770 (c)**



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 2 MPa; cooling under a pressure of 2 MPa during 10 min. Pure additive films were spin-coated from 10 g L<sup>-1</sup> chloroform solution onto polypropylene plates.

**Quality of Functionalized Probes.** Since common spectroscopic techniques are unable to characterize nanometer-sized tips, 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 alkanethiol monolayers terminating in either -CH<sub>3</sub> or -OH were measured.<sup>21</sup> The observed trend in adhesive force agrees with the chemical contrast expected on the basis of solvent exclusion effects.<sup>23,24</sup> These adhesion forces measurements between functionalized tips and model surfaces were then used as a routine operation to validate the grafting of functional groups on tips. It is worth noting that the standard deviation is more important in N<sub>2</sub> (20–25%) than in water (10–15%) due to capillary forces, which are not completely suppressed in N<sub>2</sub>.

**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<sup>-1</sup> and an integrated pyramidal tip whose apex radius was typically equal to 50 nm. All AFM measurements were performed in either nitrogen atmosphere or in 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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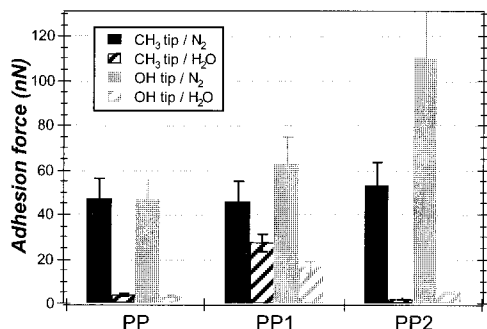
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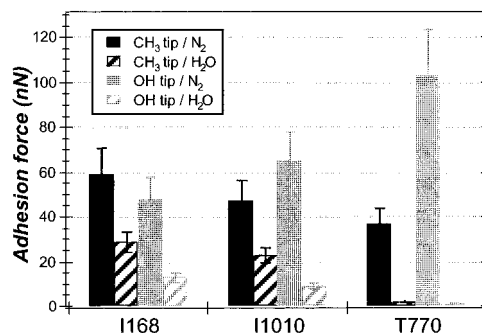


**Figure 1.** Average adhesion forces (nN) measured with  $-\text{CH}_3$ - and  $-\text{OH}$ -terminated tips on blank polypropylene (PP) and stabilized polypropylene (PP1 and PP2). PP1 contains 0.05 wt % of Irganox 1010 and 0.1 wt % of Irgafos 168. PP2 contains 0.05 wt % of Irganox 1010, 0.1 wt % of Irgafos 168, and 0.5 wt % of Tinuvin 770. The force–distance curves were recorded in water or in nitrogen atmosphere.

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. AFM force curves provide detailed information about strength of the tip–sample interaction in particular local points, but they lack the two-dimensionality of the AFM mapping. To map the distribution of adhesion forces, the method of “force volume imaging” mode was applied. In this mode an array of force curves can be obtained over the entire probed area. This technique involves taking hundreds or thousands of force curves over the course of a raster scan. Each force curve is measured at a unique  $x$ – $y$  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 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 forces correspond to the average of the values measured for at least two independent tip–sample combinations. As the adhesive interaction between tip and sample is strongly influenced by the tip diameter and the spring constant of the cantilever, each probe should be rigorously characterized before each experiment if a quantitative analysis is expected. We have noticed during our experiments that the spring constant of the cantilevers may vary until 50% and the nominal tip curvature radius of 50 nm varies in fact in the range 50–100 nm, depending on the particular batch of the manufacturer. It is thus difficult to obtain quantitative information on this basis. As the measurement of each tip diameter and spring constant would make the experiments fastidious, we have decided to use two tips with different chemical moieties in two different media to obtain an overall adhesion fingerprint. Four sets of measurements were thus carried out for each compound: pull-off forces were recorded with  $-\text{CH}_3$  and  $-\text{OH}$  terminated tips, in nitrogen atmosphere and in water. Relative adhesion data in one set of measurements can thus be compared from one sample to the other.

### 3. Results and Discussion

To explore the feasibility of detecting the presence of additives on polypropylene surfaces, adhesion force measurements were performed on 4 polypropylene samples (Figure 1). PP is not stabilized and thus contains no additives. PP1 contains only antioxidants (0.1 wt % of Irgafos 168 and 0.05 wt % of Irganox 1010). PP2 contains both antioxidants and the UV-light stabilizer (0.1 wt %



**Figure 2.** Average adhesion forces (nN) measured with  $-\text{CH}_3$ - and  $-\text{OH}$ -terminated tips on Irgafos 168, Irganox 1010, and Tinuvin 770 films spin-coated onto polypropylene. The force–distance curves were recorded in water or in nitrogen atmosphere.

of Irgafos 168, 0.05 wt % of Irganox 1010, and 0.5 wt % of Tinuvin 770). The surface roughness is of considerable importance when measuring adhesion forces. The measured pull-off force indeed depends on the contact area between the tip and the sample. A high surface roughness can thus disrupt specific interactions between the tip and the surface. The root-mean-square roughness measured on the polypropylene plates on  $10 \times 10 \mu\text{m}$  images was around 3–5 nm. Recently, Schönherr et al. have investigated polymer film surfaces with a mean roughness of 8 to 20 nm and their results suggest that such a roughness does not significantly disrupt the pull-off forces measured by CFM.<sup>15,17</sup> Thus we do not expect influence of the sample topology on the adhesion force measurements in the present case.

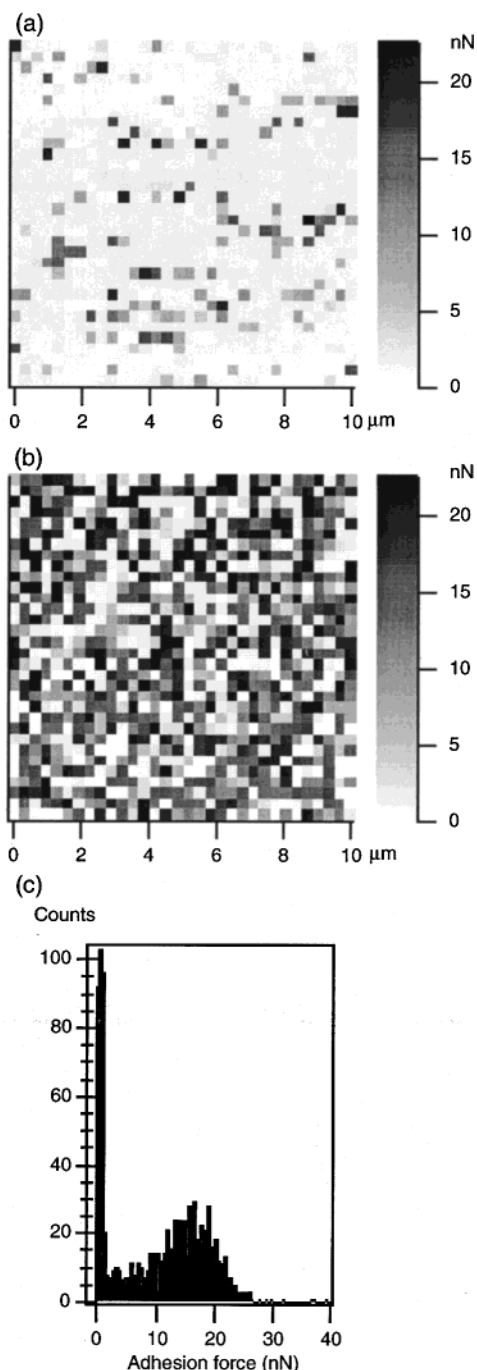
**Polypropylene Free from Additive.** The pull-off forces obtained in water on PP are unexpectedly low. As shown in Figure 1, a  $-\text{CH}_3$ -terminated tip brought into contact with the polypropylene surface exhibits a pull-off force of 4 nN, and an  $-\text{OH}$ -terminated tip brought into contact with the same surface exhibits a pull-off force of 3 nN. A pure polypropylene surface is hydrophobic<sup>14</sup> and is expected to behave almost like a  $-\text{CH}_3$ -terminated surface. Since water does not wet hydrophobic methyl-terminated surfaces, a strong force is needed to break the tip–sample contact (solvent exclusion effect). On the contrary, water wets hydrophilic surfaces and weaker forces suffice to break the tip–sample interaction.<sup>24</sup> We thus expected to observe a high pull-off force when using a  $-\text{CH}_3$ -terminated tip in water on the PP sample. On the contrary, the adhesive behavior that we observe in water is similar to the one observed on oxyfluorinated or on UV–ozone-treated polypropylene films and is typical of a more or less hydrophilic polypropylene surface.<sup>16,18</sup> It is not surprising, as it is well-known that polypropylene oxidizes very rapidly during material processing if it is not stabilized.<sup>25,26</sup> The adhesive signature that we observe is thus probably that of an oxidized polypropylene surface.

**Polypropylene Stabilized With Antioxidants.** PP1 shows a more hydrophobic behavior (Figure 1). It is the expected behavior for a nonoxidized polypropylene surface. But this behavior can also be induced by the presence of antioxidants at the surface. As a comparison, adhesion forces were recorded on Irgafos 168 and Irganox 1010 films obtained by spin-coating onto polypropylene (Figure 2). Both additives show a similar behavior, linked to their

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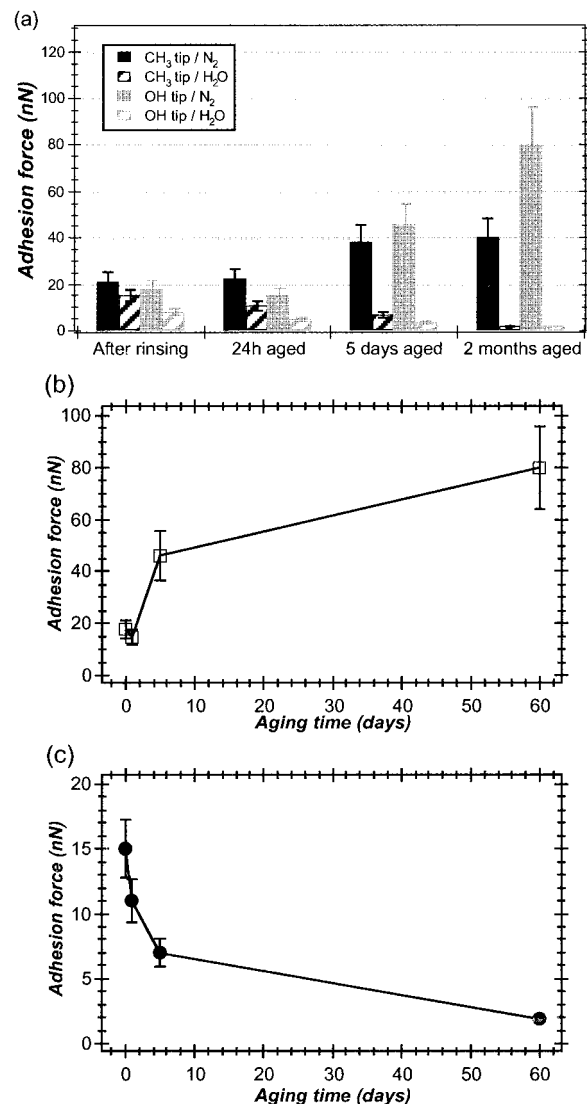
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**Figure 3.** (a) Typical adhesion map obtained on PP2 (0.05 wt % of Irganox 1010, 0.1 wt % of Irgafos 168, and 0.5 wt % of Tinuvin 770) with a  $-\text{CH}_3$ -terminated tip in water. Dark color indicates high adhesion, and bright color indicates low adhesion. (b) Adhesion map obtained on a few regions of the PP2 surface with a  $-\text{CH}_3$ -terminated tip in water. (c) Histogram of adhesion force distribution corresponding to the adhesion map in panel b.

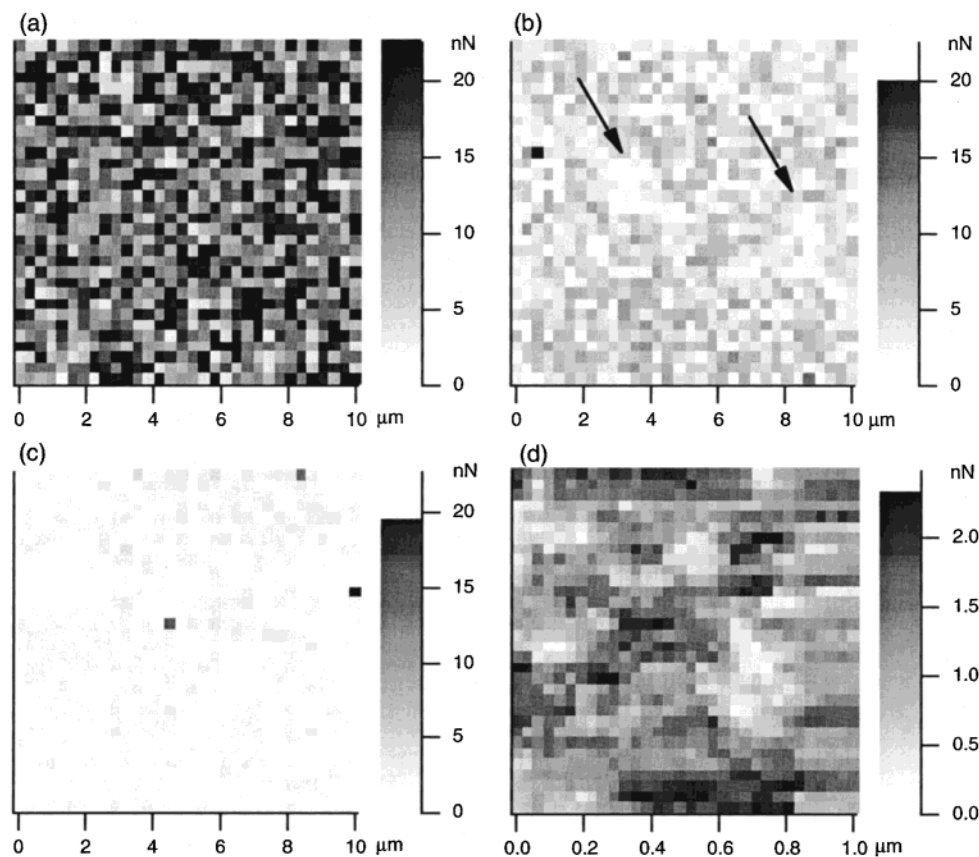
chemical structure (Chart 1). Irgafos 168 and Irganox 1010 cannot be distinguished because of their too similar response toward the probes. The signature is that of a hydrophobic system, as the adhesion force obtained in water is rather strong. This behavior is probably due to the numerous *tert*-butyl groups present on these compounds. These *tert*-butyl groups are indeed very bulky and probably mask the rest of the molecule. The signature that we observe for PP1 is very similar to the one of the pure additives. This signature is thus either that of pure nonoxidized polypropylene or that of the antioxidants.



**Figure 4.** (a) Average adhesion forces (nN) obtained with  $-\text{CH}_3$ - and  $-\text{OH}$ -terminated tips on PP2 (0.05 wt % of Irganox 1010, 0.1 wt % of Irgafos 168, and 0.5 wt % of Tinuvin 770) after rinsing with chloroform and dichloromethane and on the same surface 24 h, 5 days, and 2 months after rinsing. The force-distance curves were recorded in water or in nitrogen atmosphere. (b, c) Evolution of the average adhesion force measured with an  $-\text{OH}$ -terminated tip in nitrogen (b) and with a  $-\text{CH}_3$ -terminated tip in water (c) as a function of the aging time. The solid lines have been added as a guide to the eye.

The presence of both antioxidants on the surface has been confirmed by ToF-SIMS analysis.<sup>21</sup>

**Polypropylene Stabilized with Antioxidants and UV-Light Stabilizers.** The signature observed for PP2 is very different from the one observed for PP1 (Figure 1). The adhesion force obtained when using a  $-\text{CH}_3$ - and an  $-\text{OH}$ -terminated tip in water is low (1.8 and 5 nN, respectively). This adhesive behavior in water is typical of a hydrophilic surface. As we do not observe a hydrophilic behavior for the polymer containing both antioxidants in the same concentration (PP1), we cannot attribute this hydrophilic behavior to an oxidized polypropylene surface. 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 (Figure 2). The surface of PP2 is thus probably composed of a layer of Tinuvin 770. Adhesion forces obtained on a Tinuvin 770 film spin-coated onto polypropylene are reported in Figure 2. The behavior is very different from the one observed for



**Figure 5.** Adhesion maps obtained on PP2 (0.05 wt % of Irganox 1010, 0.1 wt % of Irgafos 168, and 0.5 wt % of Tinuvin 770) after rinsing with chloroform and dichloromethane (a), 5 days after rinsing (b), 2 months after rinsing (c, d) with a  $-\text{CH}_3$ -terminated tip in water. Dark color indicates high adhesion, and bright color indicates low adhesion. Arrows indicate the appearance of areas corresponding to low adhesion forces. Note the different gray scale in panel d.

the antioxidants (Figure 2). Tinuvin 770 has a surfactant-like structure. It is made of a hydrophobic alkyl chain and a hydrophilic head. It seems to behave like a hydrophilic system, as the adhesion force measured in water is low using both tips and the adhesion force measured with an  $-\text{OH}$ -terminated tip in nitrogen is high. The overall behavior of the polypropylene surface on which a film of Tinuvin 770 has been spin-coated (Figure 2) is very similar to the one observed for the PP2 surface (Figure 1). This similarity suggests that Tinuvin 770 is present on the surface of PP2.

The adhesion map in Figure 3a has been obtained with a  $-\text{CH}_3$  tip in water. This is the tip–environment combination that gives the best contrast in pull-off forces between PP, PP1, and PP2. This image shows the lateral distribution of pull-off forces. The great majority of pull-off forces in Figure 3a correspond to a low adhesion force, around 1 nN (bright color). This is close to the typical adhesion force measured on Tinuvin 770 (1.8 nN). Small areas present a higher pull-off force (10–20 nN). They can be interpreted as 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  $1.5\text{ }\mu\text{m}$ . The major part of the surface area is thus covered by an external layer of Tinuvin 770, and the average adhesion force measured by CFM corresponds to the adhesion force obtained on pure Tinuvin 770. A few regions of the PP2 surface are not so densely covered by Tinuvin 770, as illustrated in Figure 3b. Bright areas correspond to adhesion forces around 1 nN and dark areas to adhesion forces between 10 and 20 nN. The distribution of adhesion forces shows two maxima around 1 and 16 nN (Figure 3c). It reveals that in this area the surface is made

of Tinuvin 770 islands on either pure polypropylene or antioxidants.

The presence of Tinuvin 770 on the PP2 surface was confirmed by ToF–SIMS analysis.<sup>21</sup> Peaks corresponding to fragments belonging to both other additives (Irganox 1010 and Irgafos 168) also appear in the ToF–SIMS spectra. The three additives, initially contained in the bulk of the polymer, are thus present on the surface after material processing. ToF–SIMS measurements qualitatively show that the three additives are present on the surface. CFM mapping also confirms the presence of the three additives, but it enables the characterization of their submicrometer spatial distribution and evidences that Tinuvin 770 is the main component of the surface. It is not surprising, as Tinuvin 770 is not very soluble in polypropylene. It is thus rejected by the polymer matrix.

The PP2 surface was then rinsed with chloroform and dichloromethane, which are good solvents of the additives. The washed surface (Figure 4a) shows a remarkable change in adhesion from the initial PP2 surface. The average adhesion force obtained in water with a  $-\text{CH}_3$  tip is equal to 15 nN. The surface behaves thus more like a hydrophobic polypropylene surface. This surface behavior is also very different from that of pure PP surface (Figure 1), confirming our previous conclusion that the PP surface was oxidized. In PP2, the additives have protected the polymer against oxidation during its processing. An adhesion map obtained in water with a  $-\text{CH}_3$  tip is shown in Figure 5a. This image shows higher average adhesion force than in Figure 3a. The areas of small adhesion forces can be interpreted as areas where there is some Tinuvin 770 that reappears at the surface. It is indeed known from ToF–SIMS investigations that the additive segregation

for Tinuvin 770 is extremely fast.<sup>27</sup> Kersting et al. have shown that Tinuvin 770 is already detected after about 10 min on a rinsed sample.<sup>27</sup> As the CFM measurements are performed after an equilibration time of about 1 h, it is understandable that some Tinuvin 770 is detected. This washed surface was then allowed to age in air, and adhesion forces were again measured after 24 h, 5 days, and 2 months (Figure 4a). The surface shows a time dependence in adhesion force measurements. The average pull-off force measured with an -OH-terminated tip in nitrogen increases (Figure 4b), whereas the average pull-off force measured with a -CH<sub>3</sub>-terminated tip in water decreases as a function of aging (Figure 4c). It means that the surface becomes more and more hydrophilic during aging. The behavior of the 2-month-aged surface is very similar to the one observed for the PP2 surface. It means that an outermost layer of Tinuvin 770 has reappeared on the surface. The additives contained in the bulk of the material have migrated toward the surface. The adhesion maps obtained in water with a -CH<sub>3</sub> tip are shown in Figure 5b,c. Islands of low adhesion forces (indicated by arrows) appear on the 5-day-old sample. The 2-month-old sample shows a homogeneous distribution of low adhesion forces that can be attributed to the presence of Tinuvin 770. The surface is in fact rather heterogeneous on a smaller scale. The 1 × 1 μm adhesion map (Figure 5d) shows islands of very low adhesion forces. This image has been recorded at a resolution of 32 × 32 pixels; measurements were thus taken at about 30 nm intervals. The adhesion force resolution is lower than 0.2 nN. The higher adhesion force corresponds to 2.4 nN, and the lower, to 0.1 nN. These small variations could be due to variations in the thickness of the Tinuvin 770 overlayer or to different arrangements of the Tinuvin 770 molecules. If the aged surface is washed again, it recovers a hydrophobic behavior, proving the fact that the appearance of the hydrophilic behavior due to aging is related to additive migration toward the surface and not to polymer oxidation.

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#### 4. Concluding Remarks

We have shown in this contribution that AFM tips functionalized with alkanethiol SAMs can be utilized to map the distribution of adhesion forces on polypropylene surfaces. We have compared local adhesion forces on blank polypropylene, polypropylene containing antioxidants, and polypropylene containing antioxidants and UV-light stabilizers, using -CH<sub>3</sub>- or -OH-terminated tips. These chemically specific forces were shown to correlate with the presence of additives at the surface. We were able to evidence that additives migrate toward the surface and to obtain adhesion maps. Laterally resolved adhesion force maps gave evidence for a modification of additive distribution on the surface due to material aging.

We have thus presented a powerful application of chemical force microscopy to map aging effects on polymer surfaces on the basis of the detection of additives. The method is rather simple and can be very useful for detecting local adhesion defects or chemical heterogeneities on common polymer surfaces as well as on organic layers at the sub-100 nm scale. AFM investigations are now underway to compare adhesion maps and topographical features on regular AFM images to correlate the location of additives and the presence of amorphous and lamellar regions of the surface.

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