

Improved Polyimide/Metal Adhesion by Chemical Modification Approaches

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ABSTRACT: To increase their adhesion to silver, polyimide (PI) surfaces were modified by sulfonation reactions by means of different experimental procedures. The results of these modification reactions were analyzed in terms of the variation of the surface chemical composition examined by X-ray photoelectron spectroscopy. Long-time reactions were also followed by monitoring the increase in weight of the PI films. Changes in the total surface free energy were evaluated by contact angle measurements with the sessil drop method. The influence of the modification reactions on silver/PI adhesion was estimated by means of a 180° peeling test according to ASTM standards. Finally, the effect of chemical modification on film roughness was investigated by means of atomic force microscopy. The results obtained showed that a net improvement, that is, over the maximum rate according to the reference ASTM test, was attained via both the gaseous SO₃ and concentrated H₂SO₄ procedures, with the latter procedure more effective in the presence of silver sulfate as a catalyst. However, the former was judged more convenient because of the low amount of reagents used and the simplicity of cleaning operations. Interestingly, optimum adhesion levels were attained after only very low contact times with all sulfonating agents, that is, after about 30 s. These results were compared with the effects on PI/silver adhesion of traditional etching procedures with KOH aqueous solutions at different temperatures. In this case, good adhesion was observed only after longer reaction times, that is, on the order of 1–2 min in the case of 1M KOH and 1 h in the case of 0.1M KOH. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1971–1985, 2001

Key words: polyimide; polymer surface modification; polymer metallization; wet procedure; sulfonation reaction; chemical etching; silver sputtering; polymer–metal adhesion

INTRODUCTION

Polyimides (PIs) are high-performance materials endowed with excellent physical and mechanical

properties over a wide range of temperatures, which make them appealing for a number of applications ranging, for instance, from high-performance composites for the aerospace industry to chip packaging for the microelectronic industry.^{1,2}

In a recent, innovative approach to low-cost superconductors, the development of silver/metalized polymeric substrates for superconducting metal oxides layers deposition was requested.

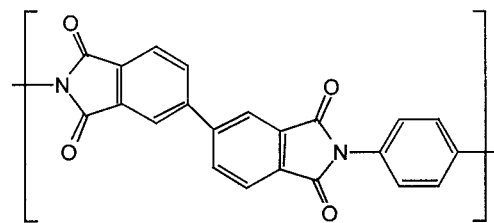
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Among the main physical requirements for a polymer to be used for the proposed application, thermal stability up to 400°C, low dielectric constants, and low coefficient of thermal expansion in a wide range of temperatures were the most relevant. The best polymeric material that matched all requirements turned to be the semiflexible, linear PI Upilex S manufactured by UBE Industries Ltd. Upilex is thermally stable up to 500°C, has a coefficient of thermal expansion of 20 ppm/°C in the range 20–200°C, and is claimed to be flexible to temperatures as low as –269°C.

One disadvantage of PIs is their poor adhesion to almost all materials^{3–5} either organic or inorganic, including other layers of the same PI. Among the most common routes for the improvement of PI metal adhesion, surface roughening⁶ and surface modification by the introduction of chemically active groups by either physical (plasma treatment, corona discharge, or X-ray, laser, ion beam, or flame treatment)⁷ or chemical procedures (etching in the presence of KOH aqueous solutions)^{8,9} have been reported. A comparison between the previously mentioned general procedures indicates, for instance, that although physical treatments are endowed with specific merits such as velocity and the possibility for implementation into a productive cycle, chemical methods ensure reproducibility, simplicity, and a low cost of operations. Moreover, the chemistry of wet-processed polymer surfaces is often more easily predicted and defined at a molecular level; after surface reactions, in most cases it is the same pattern as the corresponding reactions in the homogeneous phase.

Despite the abundance of literature reports on PI metallization processes, no specific indications were found regarding silver/PI adhesion, which led us to investigate this issue in more detail. In this article, we report, therefore, on the development of chemical modification procedures of PI surfaces for the electrophilic sulfonation reaction onto the aromatic rings of the PI repeating unit with the specific aim of improving their adhesion to silver. Several modification methods were evaluated in terms of their simplicity of execution and effectiveness. A comparison with the effects of traditional chemical etching procedures with KOH aqueous solutions on PI/silver adhesion is discussed.



UPILEX S

EXPERIMENTAL

Materials

UBE Industries Ltd. (Japan) provided the PI Upilex 50S as solvent cast and cured sheets with a thickness of 50 μm . Fuming sulfuric acid (65%) from Merck (Darmstadt, Germany), sulfuric acid (puriss) from Kebo Lab AB (Sweden), Ag_2SO_4 , sulfur trioxide–pyridine complex, and 0.1M and 1M KOH aqueous solutions from Fluka Chemie AG (Germany) were used in the surface-modification experiments.

Chemical Treatments

All chemical treatments were performed repeatedly on rectangular Upilex sheets 30 \times 40 mm in dimension. All experiments were carried out in closed glass flasks. All samples were initially cleaned with acetone before further modification. After treatment, all films were removed from the reactive solutions, rinsed twice for 3 min in deionized water and twice for 3 min in isopropanol. Finally, they were dried at room temperature for 90 min and 6 h prior to contact angle measurement and sputtering, respectively.

Sulfonation Reaction with Fuming Sulfuric Acid

PI films were immersed into 65% fuming sulfuric acid at 0 or 20°C for 20, 40, or 60 s in experiments similar to those performed by Seita et al.¹⁰

Sulfonation Reaction with Sulfur Trioxide–Pyridine Complex Dissolved in Dimethylformamide (DMF)

A saturated solution of SO_3 –pyridine complex in dry, freshly distilled DMF was prepared and kept under nitrogen atmosphere. Modifications of PI films were performed at 80°C for 1 h and 100°C for 1 or 5 h.

Sulfonation Reaction with Sulfur Trioxide–Pyridine Complex Dispersed in Pyridine

A couple of tablespoons of SO_3 -pyridine complex was added to dry, freshly distilled pyridine and kept under nitrogen. The mixture was then heated up to 100°C . PI films were put in contact with the reactive solution for 15 h.

Sulfonation Reaction in Concentrated Sulfuric Acid with and Without Ag_2SO_4 Catalysis

PI films were immersed in concentrated (96%) sulfuric acid at room temperature for different times throughout 15 h. In case of Ag_2SO_4 -catalyzed reactions, an excess of salt (400 mg in 40 mL of sulfuric acid) was added to the acid and mixed thoroughly.

Sulfonation Reaction in Gaseous Sulfur Trioxide

PI films were exposed to gaseous SO_3 environments prepared by first inserting fuming sulfuric acid (65% fuming) into a dry, closed container, then letting it equilibrate until complete saturation of the closed environment. The concentration of SO_3 in the gas phase was calculated by extrapolating data from Miles, Nipage, and Wilson¹¹ of vapor pressure over oleum to the right temperature and concentration. For 65% oleum at 20°C , the extrapolated vapor pressure is 0.066 atm given a concentration of 2.75 mM SO_3 in the gas phase. Modifications were carried out at room temperature with 65% oleum for different periods of time up to 3 h.

KOH Etching

The method consisted in inserting PI films into aqueous solutions of different concentrations (0.1 or 1.0M) of KOH at different temperatures (30, 50, and 80°C) for different times (1, 10, and 30 min).

Silver Deposition

Silver was deposited onto the surface by a vacuum evaporation process with a JEOL vacuum evaporator JEE-4B (Jeol Electron Optics Laboratory Co., Ltd., Tokyo, Japan). The thickness of the silver layer was calculated once the weight of silver deposited and the deposition area was known. The resulting average estimated value was 50 nm.

Contact Angle Measurement

All samples were analyzed by the measurement of the contact angle between the surface and deionized water with the sessile drop method. Two advancing angles and two receding angles were measured on each drop, and each surface was analyzed with five drops, for a total of ten measurements. Both advancing and receding contact angles were reported with a 90% confidence interval.

X-Ray Photoelectron Spectroscopy (XPS)

XPS was performed on a Kratos Axis-HS instrument (Kratos Analytical, Manchester, UK) with a Mg radiation source and a 90° take-off angle with regard to the sample surface. The kind of analysis performed was an elemental sweep of the surface to determine the composition.

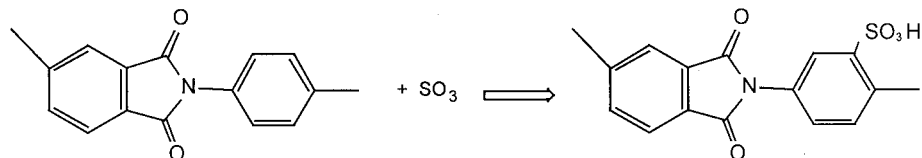
Adhesion Testing by Tape Test

Adhesion between the modified PI surfaces and vacuum-deposited silver was estimated with an ASTM "tape test."¹² A crosscut pattern consisting of 11×11 cuts, each 1 mm apart, was cut with a razor blade, a metallic cutting guide, and a ruler. A piece of Permacel polyester tape (New Brunswick, NJ) was placed over the grid. To ensure good contact between the tape and substrate, the tape was rubbed firmly with an eraser. Then, the tape was removed at an angle as close to 180° as possible. The grid area was inspected, and the following scale was used to rate the degree of adhesion:

- 5B: All cutting edges were smooth, and none of the squares were detached.
- 4B: Less than 5% of the area was detached.
- 3B: 5–15% of the area was detached.
- 2B: 15–35% of the area was detached.
- 1B: 35–65% of the lattice was removed.
- 0B: More than 65% of the lattice area was detached.

Atomic Force Microscopy (AFM)

AFM measurements were performed with a NanoScope IIIa Multimode apparatus from Digital Instruments (USA) with a scan size of 10×10 mm, a z -height of 50 nm, mode H/Ph, and a scan rate of 1.5 Hz.



Scheme 1

RESULTS AND DISCUSSION

Chemical Modifications of PI Surfaces

A general procedure for the improvement of PI/metal adhesion is the modification of their surfaces through methods capable of increasing their hydrophilicity, that is, of increasing their total surface free energy. Effective PI metallization has been attained in a number of reported cases after the modification of PI surfaces via either chemical etching with KOH solutions or oxygen plasma treatment. Among others, examples of successful coating with gold,¹³ copper,⁴ chromium/copper,¹⁴ and tin/palladium have been reported. However, we found no specific data on silver metallization of PI, which led us to investigate this issue in some detail. A number of different chemical modifications of PI surfaces were developed and compared in terms of effectiveness and reproducibility, as well as simplicity of execution. Two main classes of chemical reactions were considered, the first one involving electrophilic substitutions to the aromatic rings contained in the PI repeating units, namely, sulfonation reactions (e.g., Scheme 1) and the second one consisting of the etching of PI surfaces with KOH aqueous solutions (see Scheme 2) that caused hydrolysis of the PI imido groups.

Sulfonation Reactions

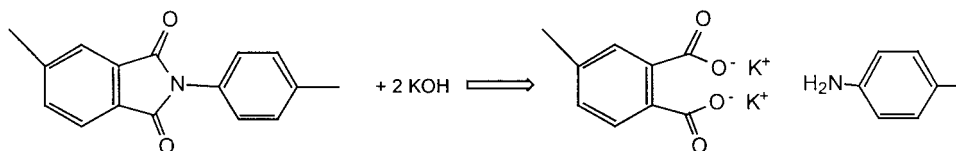
Sulfonation reactions of polymers are a common issue in polymer science. Sulfonated ionomers are used industrially for the production of compatible blends of immiscible polymers, ion exchange materials, membranes for reversible osmosis, and ul-

trafiltration, plasticizers, and conductive composites.¹⁵ The sulfonation of polymers has also been performed for the direct metallization of flexible printed circuits.¹⁰

Sulfonating reagents can be separated into three groups: (1) electrophilic reacting agents, such as sulfuric acid, oleum, free sulfur trioxide and its complexes, and halogen derivatives of sulfuric acid; (2) nucleophilic agents, such as sulfites, hydrogen sulfites, and sulfur dioxide that react with halogen derivatives and unsaturated compounds; and (3) radically reacting agents, such as sulfonylchloride (SOCl_2) and blends of gases ($\text{SO}_2 + \text{Cl}_2$, i.e., sulfochloration, or $\text{SO}_2 + \text{O}_2$, i.e., sulfoxidation).

The most important industrial sulfonation process, which produces sulfonated compounds for detergents, is based on the heterogeneous reaction with SO_3 as the sulfonating agent and fatty acids as the substrate. Heterogeneous sulfonation of polymers has been carried out by a number of researchers. For example, Seita et al. sulfonated PI films with fuming sulfuric acid.¹⁰ Heterogeneous sulfonation of PET, LDPE, HDPE, and PP above 30% fuming sulfuric acid has been performed by Kang et al.¹⁶

The sulfur trioxide-pyridine complex shows low solubility in nearly all common solvents. It is insoluble in pyridine, nitrobenzene, cyclohexane, chloroform, acetone, and so on at room temperature. It is soluble in DMF. Sulfur trioxide-pyridine has been used extensively as a laboratory reagent for sulfating amines and proteins and for sulfonating acid-sensitive heterocyclic compounds and alkenes. Reactions are usually



Scheme 2

Table I Contact Angle of PI Surfaces with Water After Modification with Different Sulfonating Agents

| | Fuming Sulfuric Acid | | | SO ₃ -Pyridine Complex in DMF | | | SO ₃ -Pyridine Complex in Pyridine | |
|-----------|----------------------|--------|--------|--|--------|--------|---|--------|
| | Time (s) | 0°C | 20°C | Time (min) | 80°C | 120°C | Time (min) | 100°C |
| Advancing | 0 | 76 ± 1 | 76 ± 1 | 0 | 76 ± 1 | 76 ± 1 | 0 | 76 ± 1 |
| | 20 | 46 ± 4 | | 60 | 71 ± 1 | 71 ± 1 | 120 | 70 ± 2 |
| | 40 | | 42 ± 5 | 300 | | 70 ± 1 | | |
| Receding | 0 | 44 ± 1 | 44 ± 1 | 0 | 44 ± 1 | 44 ± 1 | 0 | 44 ± 1 |
| | 20 | 19 ± 3 | | 60 | 37 ± 3 | 36 ± 3 | 120 | 41 ± 3 |
| | 40 | | 25 ± 4 | 300 | | 36 ± 1 | | |

carried out with excess pyridine or in the presence of a solvent at temperatures below 120°C.

In this study, sulfonation reactions were carried out according to four different procedures, namely, by direct contact with fuming sulfuric acid, with concentrated sulfuric acid in the presence and in the absence of added catalysts, with the SO₃-pyridine complex, and finally with SO₃ in the gas phase. The results of the modification tests, executed as described in the Experimental section, were preliminary evaluated by means of contact angle measurements with water to get a first general indication on the extent of modification related to the variation in surface free energy. Those methods leading to the most interesting results were then investigated more thoroughly.

Fuming Sulfuric Acid

Fuming sulfuric acid is a violent sulfonating agent. Dipping PI films in it caused irreversible damage after contact times on the order of seconds. Nevertheless, contact angles between treated PI surfaces and water were measured, and the corresponding values are reported in Table I. A significant variation between contact angles before and after treatment with fuming sulfuric acid was observed, which indicated a certain variation in the surface chemical composition. However, spot measurements carried out throughout all surfaces showed an extensive surface inhomogeneity. Because of these serious inconveniences, the method was not further considered.

Sulfur Trioxide-Pyridine Complex

Treatment of PI films with a SO₃-pyridine complex dissolved in dry DMF at two different tem-

peratures (80 and 120°C) and times varying in the range 0–5 h, led to only slight decreases in contact angle values. For this reason, the initial procedure was modified by dispersing the SO₃-pyridine complex in pyridine under anhydrous conditions and heating it to 100°C to release free SO₃. PI films treated according to this procedure for 2 h showed again only a slight decrease in contact angles values, probably because of the low SO₃ concentration attained. Both methods were, therefore, not investigated further.

Concentrated Sulfuric Acid with and Without Ag₂SO₄ Catalysis

One of the easiest sulfonation methods consists of dipping the substrate material in concentrated sulfuric acid, but Ag⁺ ion is known to catalyze the sulfonation of aromatic compounds¹⁷ and at the same time decrease the amount of side reactions. Because of these premises, PI surface modification was performed in this work with either plain concentrated sulfuric acid (96%) or concentrated sulfuric acid compounded with Ag₂SO₄, as reported in the Experimental section. Percent weight variation of modified PI films and water contact angles (both advancing and receding) as a function of contact time within a wide time interval were measured. Typical results obtained are presented in Figures 1–3 for both types of sulfuric-acid-based experiments. It is apparent from results reported in Figure 1 that in all cases, PI film weight increased steadily, although with a low tempo during the first reaction steps and with a higher and constant derivative above a 90-min contact time. The almost linear trend of the weight versus time square root curves, although with different segments slopes, might suggest a dependence of the modification reaction on re-

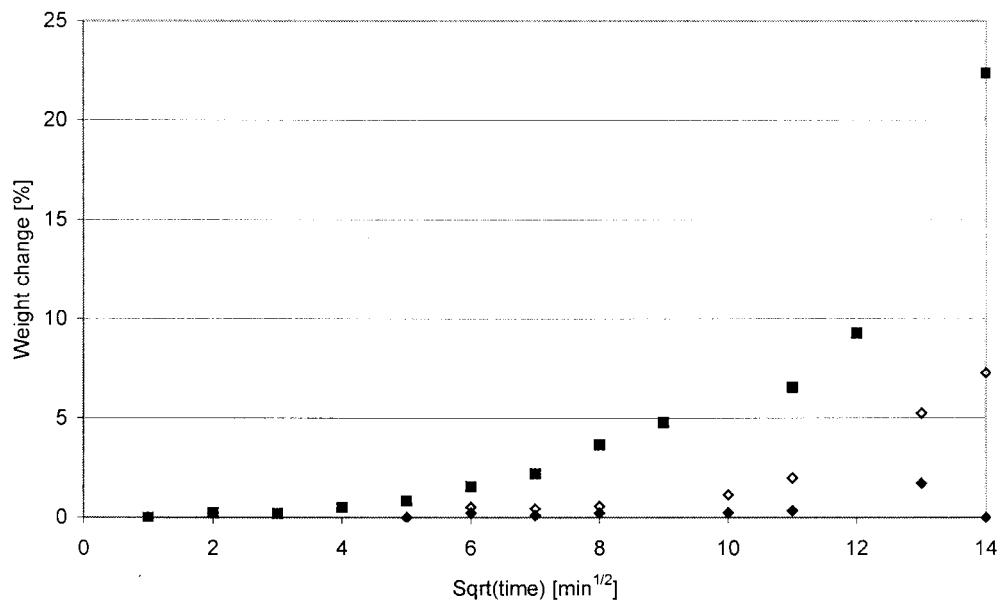


Figure 1 Increase of weight (%) with the square root of time for Upilex film modified with 96% H₂SO₄ (◆) compared to film modified with 96% H₂SO₄ and a catalyst (Ag₂SO₄; ◇) and with SO₃ above fuming sulfuric acid (■).

agent diffusion. A comparison between the effects of the two different treatments shows a much faster increase in weight in the case of Ag₂SO₄-catalyzed reactions. Figures 2 and 3 show a neat decreasing trend in contact angle from the very

first reaction steps (a significant variation was observed after only 30 s) up to a critical point when the angle rapidly increased followed by a further decrease. This first relevant discontinuity point, confirmed by several repeated experiments,

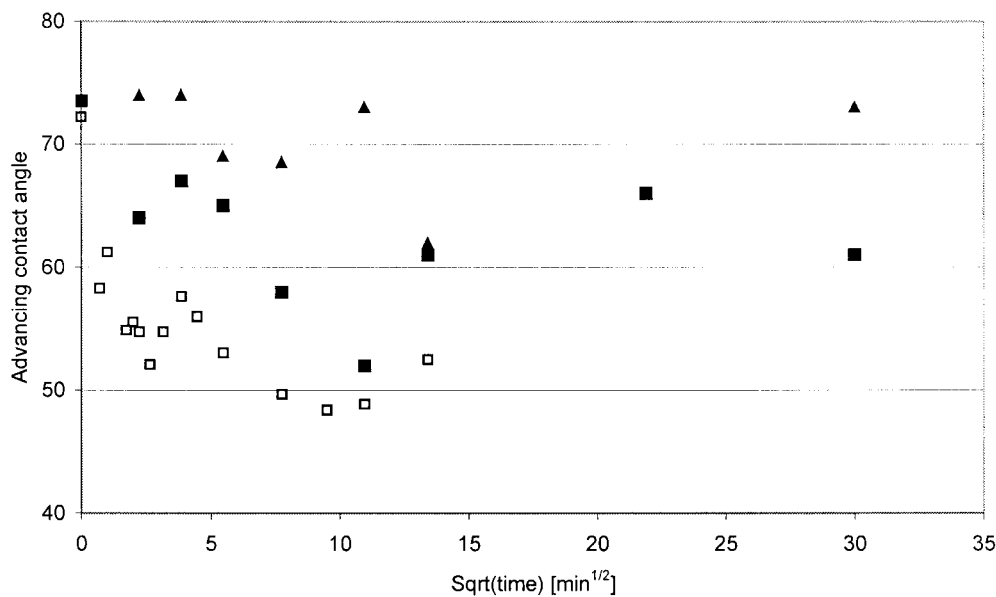


Figure 2 Variation with the square root of time of advancing angles for Upilex film modified with 96% H₂SO₄ (▲) compared to film modified with 96% H₂SO₄ and a catalyst (Ag₂SO₄; □ and ■ from different experiments).

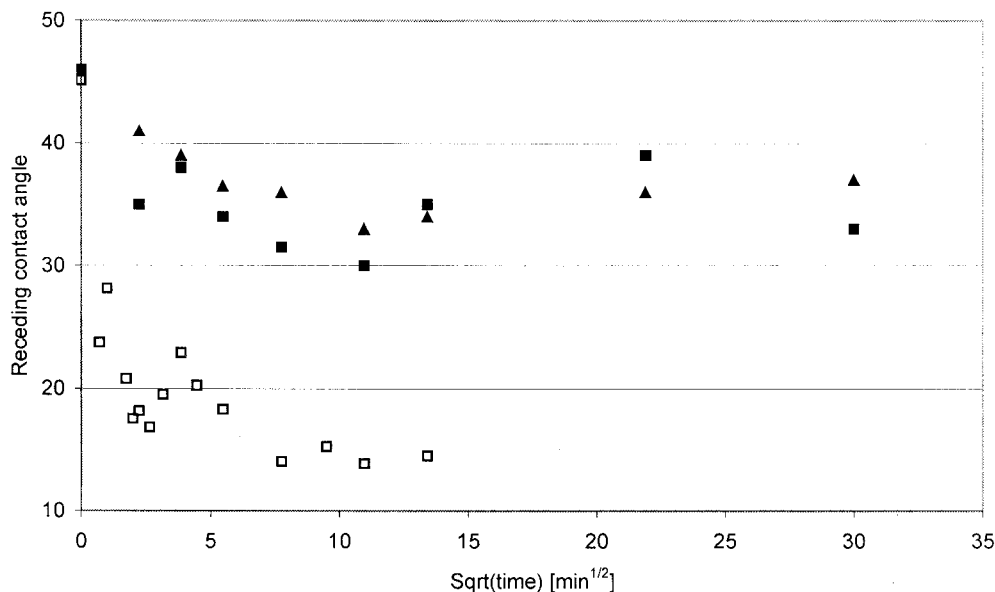


Figure 3 Variation with the square root of time of receding angles for Upilex film modified with 96% H_2SO_4 (▲) compared to film modified with 96% H_2SO_4 and a catalyst (Ag_2SO_4 ; □ and ■ from different experiments).

occurred always in coincidence with the rapid increase in sample weight observed in Figure 1. A qualitative explanation of this phenomenon could be that in correspondence of the discontinuity point, the bulk absorption of sulfonating agent started, followed by massive modifications in the bulk, which influenced the conformational status of PI surfaces.

Finally, for the sake of clarity, we report in both Figures 2 and 3 two different examples of contact angle/time square root curves obtained in two repeated experiments. These show the fair reproducibility of contact angle measurements, in line with what was already known from our previous experience on contact angle measurements, which turned out to be tremendously dependent on a number of factors, for example, surface flatness and morphology. Despite this fact, the amount of collected data allowed us to draw the final conclusion that faster modification rates occurred in cases of Ag_2SO_4 -catalyzed experiments.

Gaseous Sulfur Trioxide

Sulfonation of a solid film in gas phase is an interesting alternative to modifications with wet chemistry because of the lower amount of reagents used and the easier cleaning operations. Sulfur trioxide is known to be a strong sulfonat-

ing agent, and for this reason, PI modification experiments were also performed in 0.066-atm SO_3 environments, as described in the Experimental section. The results of weight variation curves for long reaction times showed a faster weight uptake than in the case of the concentrated sulfuric acid experiments (see Fig. 1). Figures 4 and 5 show, even in the case of the gaseous SO_3 sulfonation reactions, a neat decreasing trend in contact angle from the very first reaction steps (after maybe 10–30 s) up to a critical point when the slope suddenly decreased to zero or very close to zero. In correspondence of the same time value, the sample weight suddenly started increasing rapidly and linearly as shown in Figure 1.

Adhesion Testing

The results of preliminary modification experiments led to the conclusion that the most effective PI were those performed in the presence of concentrated sulfuric acid, including the one based on silver sulfate and the gas phase modification with SO_3 , and for this reason, they were investigated in some detail. The results of adhesion tests, carried out according to the tape test as described in the Experimental section, are reported in Table II for PI films modified either with uncatalyzed or Ag_2SO_4 -catalyzed concentrated

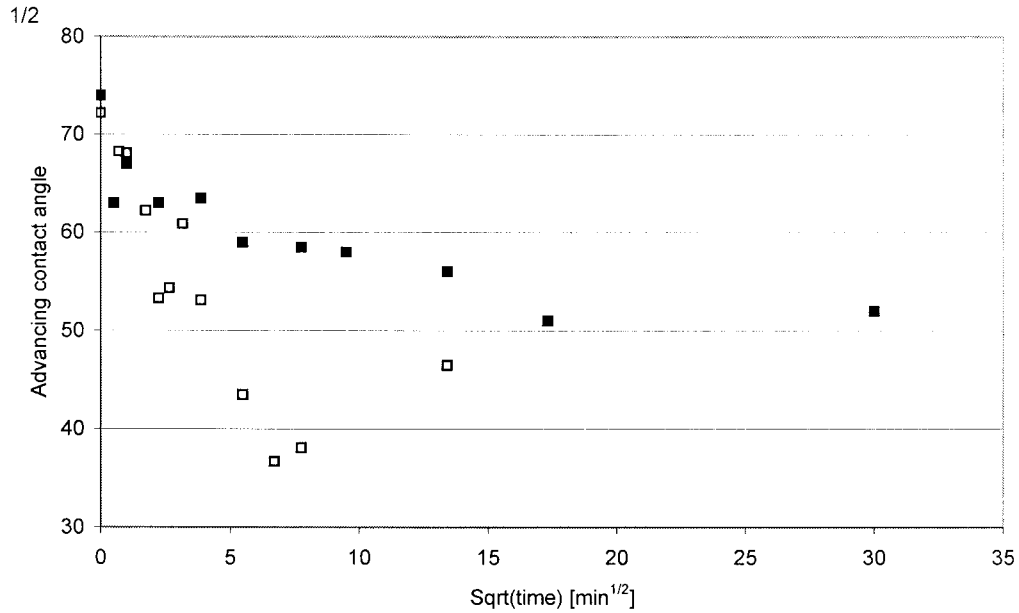


Figure 4 Advancing contact angles for Upilex films modified with SO₃ above fuming sulfuric acid (□ and ■ from different experiments).

H₂SO₄ and for SO₃-modified PI. The most interesting result of adhesion testing, which also represents the most relevant finding of this research work, is that optimum adhesion was reached in all cases, even after very short times, maybe less than 30 s. On the other hand, contact angle measurements had previously shown considerable surface free energy changes from the first reaction stages.

XPS

XPS measurements on surfaces modified with either uncatalyzed or Ag₂SO₄-catalyzed concentrated H₂SO₄ and with SO₃ were run, and the results are reported in Table III. XPS measurements in case of SO₃ were performed only after short modification times (up to 15 min) because this interval had proven to be sufficient for im-

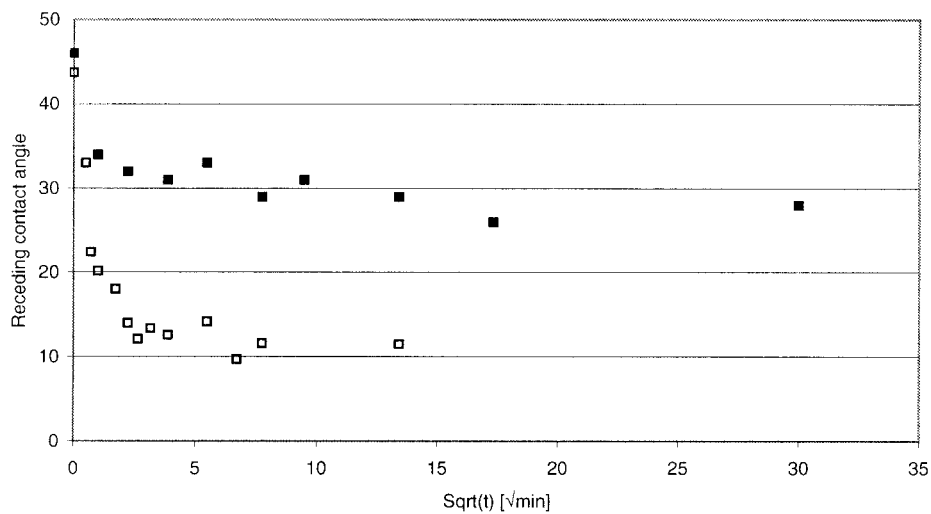


Figure 5 Receding contact angles for Upilex films modified with SO₃ above fuming sulfuric acid (□ and ■ from different experiments).

Table II Adhesion Tests on Modified PI Surfaces

| Time (min) | Adhesion Rating | | | Time (min) |
|------------|--------------------------------|--|-----------------|------------|
| | H ₂ SO ₄ | H ₂ SO ₄ + Ag ₂ SO ₄ | SO ₃ | |
| 0 | 0B | 0B | 0B | 0 |
| 0.5 | — | 5B | 5B | 0.5 |
| 5 | 4B | 5B | 5B | 5 |
| 15 | — | 5B | 5B | 30 |
| 30 | — | 5B | 5B | 60 |
| 60 | 4B | 5B | 5B | 180 |

parting a good PI/silver adhesion. All results reported in Table III show no major changes in chemical surface composition, although all other experimental evidence, such as the constant weight uptake with contact time, the distinct surface free energy increase, and the excellent metal adhesion observed in the specific tests even after short contact times, were clear indications of the occurrence of PI chemical modification.

These unexpected results initially led us to suspect a dependence of the positive adhesion trend only on a more efficient surface cleaning after contact with acids. On the other hand, extensive surface cleaning in an ultrasonic bath with different solvents carried out on unmodi-

fied PI films confirmed their poor silver adhesion. A number of hypotheses can be provided to at least qualitatively explain this observed phenomenon:

1. The occurrence of surface conformational rearrangements might have masked the introduced sulfonic groups and made them less visible by XPS analysis.
2. The adopted rinsing procedures with water and alcohols might have washed away the first modified surface monolayers and left on the top of PI films only traces of sulfur. It must be emphasized, here, that prolonged sulfonation times had already proved that PI sulfonation products dissolved completely in organic solvents.
3. Sulfonation reactions might have not taken place as the electrophilic substitution at the aromatic ring but instead followed alternative routes, such as the opening of the imido group that might have led, after the washing with water, to the formation of carboxylic acids as final reaction products.

An exhaustive interpretation of all chemical phenomena that occurred at PI surface would require deeper surface composition analyses, which is outside the scope of this work. Nevertheless,

Table III Atomic Ratios in the Surface of Upilex Surfaces Treated with Sulfuric Acid as Measured by XPS

| Time (min) | Atom Composition (%) | | | | | | | | | | | |
|--|--------------------------------|-------|------|-------|--|-------|------|------|-----------------|-------|------|-------|
| | H ₂ SO ₄ | | | | H ₂ SO ₄ + Ag ₂ SO ₄ | | | | SO ₃ | | | |
| | C | O | N | S | C | O | N | S | C | O | N | S |
| 0 | 0.080 | 0.168 | | 0 | | | | | 0 | 0 | | 0 |
| 0.5 | | | | | 80.05 | 13.55 | 6.39 | 0 | 0.080 | 0.168 | | 0 |
| 1 | 0.067 | 0.192 | | 0 | | | | | 0.067 | 0.173 | | 0.002 |
| 5 | 0.071 | 0.160 | | 0.001 | 79.57 | 14.82 | 5.61 | 0 | 0.073 | 0.181 | | 0.003 |
| 10 | 0.080 | 0.192 | | 0.006 | | | | | 0.075 | 0.170 | | 0.001 |
| 15 | 0.070 | 0.185 | | 0 | 81.11 | 13.27 | 5.62 | 0 | | | | |
| 20 | 0.080 | 0.178 | | 0 | | | | | | | | |
| 30 | | | | | 80.96 | 13.11 | 5.93 | 0 | | | | |
| 60 | 0.072 | 0.181 | | 0 | | | | | | | | |
| Theoretical | 78.57 | 14.28 | 7.14 | 0 | 78.57 | 14.28 | 7.14 | 0 | 78.57 | 14.28 | 7.14 | 0 |
| Theoretical (1 SO ₃ H × r.u.) | 68.75 | 21.88 | 6.25 | 3.12 | 68.75 | 21.88 | 6.25 | 3.12 | 68.75 | 21.88 | 6.25 | 3.12 |

Table IV Atomic Surface Composition of PI Films Treated with Sulfuric Acid as Measured by XPS

| Time (min) | Temperature (°C) | H ₂ SO ₄ Concentration (%) | C (Atomic %) | O (Atomic %) | N (Atomic %) | S (Atomic %) |
|------------|------------------|---|--------------|--------------|--------------|--------------|
| 1 | 40 | 48 | 72.2 | 20.5 | 6.1 | 1.2 |
| 0.5 | 40 | 48 | 76.8 | 17.4 | 5.6 | 0.2 |
| 1 | 80 | 48 | 74.7 | 18.1 | 6.3 | 0.9 |
| 5 | 80 | 48 | 75.7 | 17.5 | 6.0 | 0.8 |
| 10 | 40 | 96 | 79.7 | 14.6 | 5.4 | 0.3 |
| 15 | 40 | 96 | 80.5 | 13.8 | 5.5 | 0.1 |
| 20 | 80 | 96 | 80.3 | 14.0 | 5.6 | 0.1 |
| 60 | 80 | 96 | 79.9 | 14.9 | 5.2 | 0 |
| | | Theoretical | 78.57 | 14.28 | 7.14 | 0 |
| | | Theoretical for 1 sulfonic group per repeating unit | 68.75 | 21.88 | 6.25 | 3.12 |

having this experimental problem aroused our curiosity, and we decided to perform one more set of experiments in the presence of concentrated sulfuric acid at different concentrations, temperatures, and contact times (as reported in Table IV) on PI films purposely activated to electrophilic substitution by preliminary oxygen plasma treatment. The results obtained indicated, paradoxically, that the milder the reaction conditions were, the higher the sulfur content detected on the surface was. In contrast, in case of the highest

temperature, concentration, and contact time, no sulfur was detectable on PI surfaces. This apparent contradiction can be explained by the assumption that more efficient sulfonation processes led to the solubilization of the first PI surface monolayers that disappeared either in the reacting or the washing media.

KOH

Chemical etching of PI surfaces with various basic substances is known to decrease contact an-

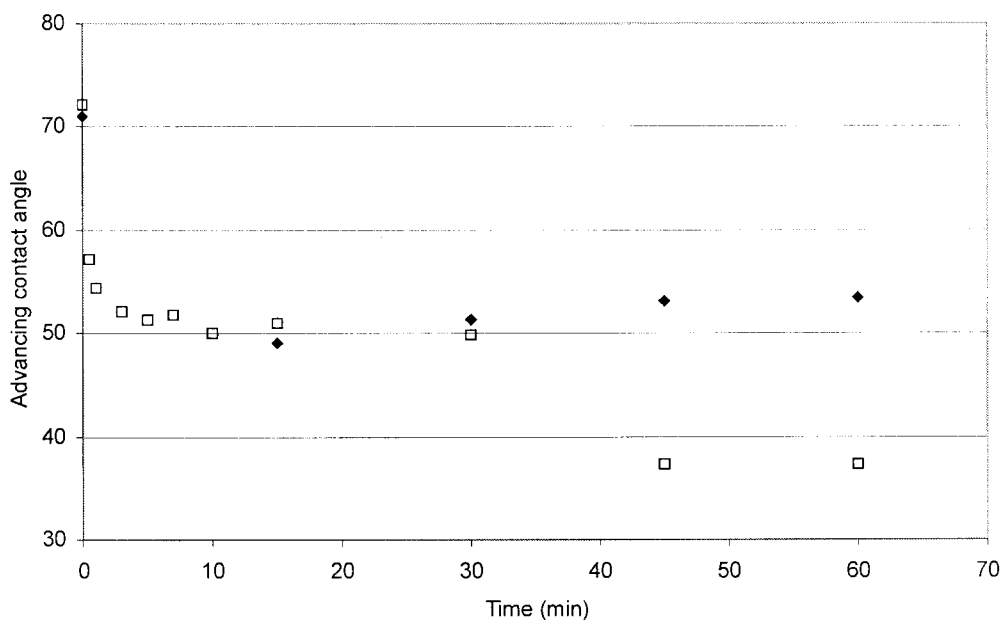


Figure 6 Advancing contact angles for Upilex 50S etched with 0.1M KOH (aqueous; ◆) and 1.0M KOH (aqueous; □).

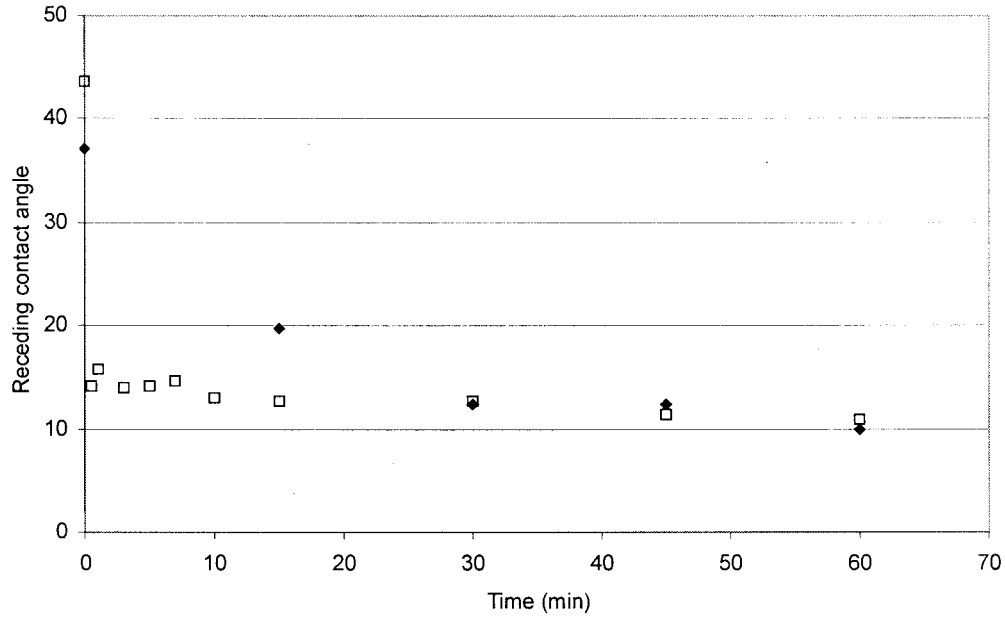


Figure 7 Receding contact angles for Upilex 50S etched with 0.1M KOH (aqueous; ◆) and 1.0M KOH (aqueous; □).

gles and, hence, increase surface energy and lead to better metal adhesion properties.^{8,9,18,19} Extensive investigations reported in the literature have clearly defined the chemical mechanism of surface reactions, which consist of the hydrolytic

cleavage of the imido groups contained in the repeating unit. In this work, PI sample modification was performed with either 0.1M or 1M aqueous KOH at different temperatures and reaction times, as reported in the Experimental section.

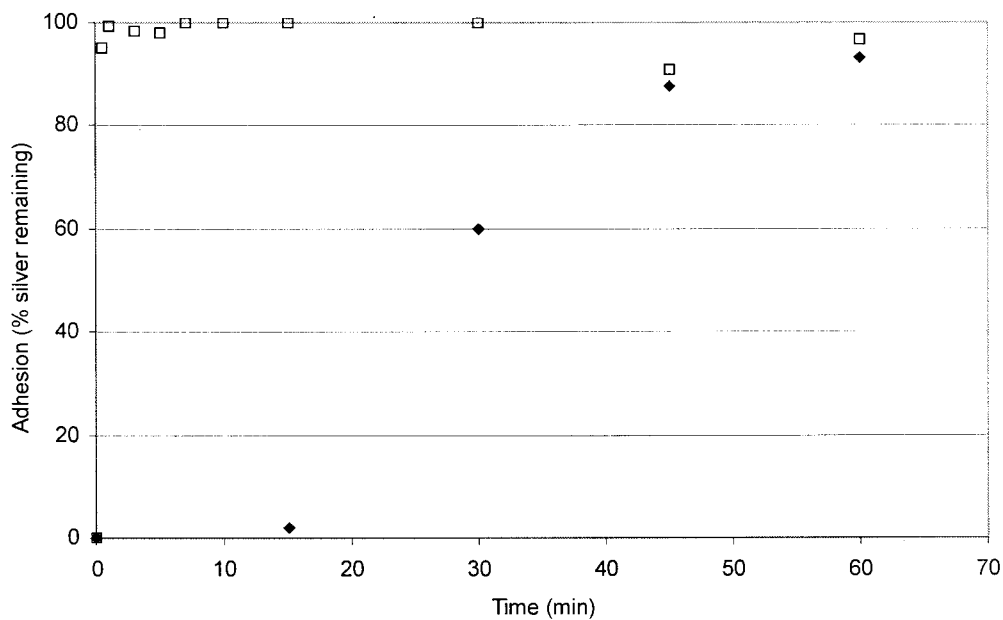


Figure 8 Adhesion, or percentage silver left on surface after tape test, for Upilex 50S etched with 0.1M KOH (aqueous; ◆) and 1.0M KOH (aqueous; □).

Table V Atomic Surface Composition of PI Films Treated with 1M KOH as Measured by XPS

| Time (min) | Temperature (°C) | C (Atomic %) | O (Atomic %) | N (Atomic %) | K (Atomic %) |
|------------|---|--------------|--------------|--------------|--------------|
| 1 | 20 | 76.3 | 16.4 | 6.5 | 0.8 |
| 1 | 50 | 74.7 | 16.8 | 6.5 | 2.0 |
| 10 | 50 | 70.1 | 19.3 | 5.8 | 4.8 |
| 30 | 50 | 70.4 | 18.6 | 5.8 | 5.2 |
| 1 | 80 | 67.3 | 20.7 | 5.7 | 6.3 |
| — | Theoretical | 78.57 | 14.28 | 7.14 | 0 |
| — | Theoretical for 100% hydrolysis to polyamide | 68.75 | 18.75 | 6.25 | 6.25 |

Typical results of contact angle measurements on PI surfaces etched with KOH are reported in Figures 6 and 7. In agreement with literature reports, the hydrophilicity of PI surface greatly increased with contact time. The results of adhesion testing are reported in Figure 8 for experiments with both 0.1M and 1M KOH solutions. The

most interesting result obtained here is that optimal adhesion was reached only after 1–2 min application at room temperature in the case of 0.1M KOH and after only 1 h with 0.1M KOH, which turned out to be somewhat higher than the corresponding times observed in sulfonation reactions. The results of XPS analysis

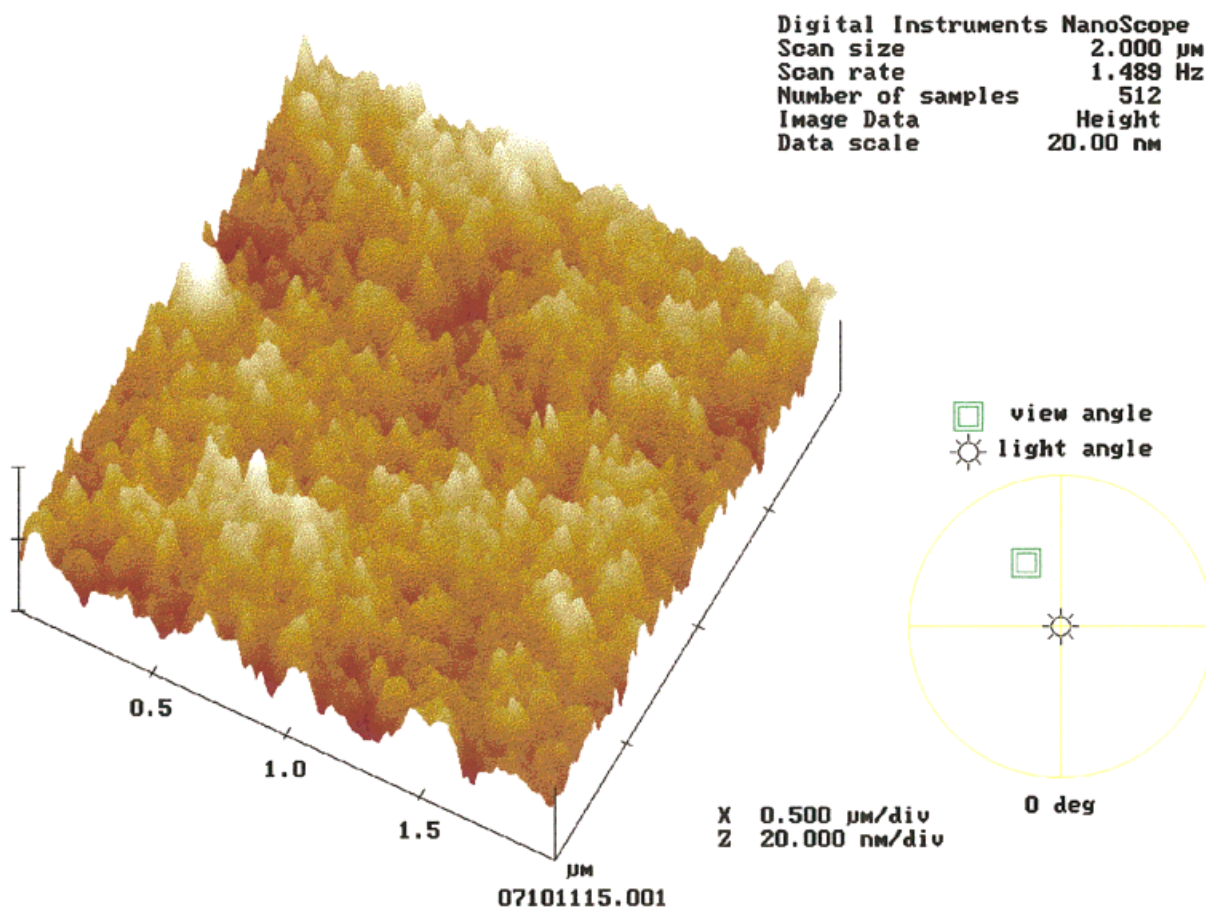


Figure 9 Atomic force micrograph of an untreated Upilex surface ($2 \times 2 \mu\text{m}$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

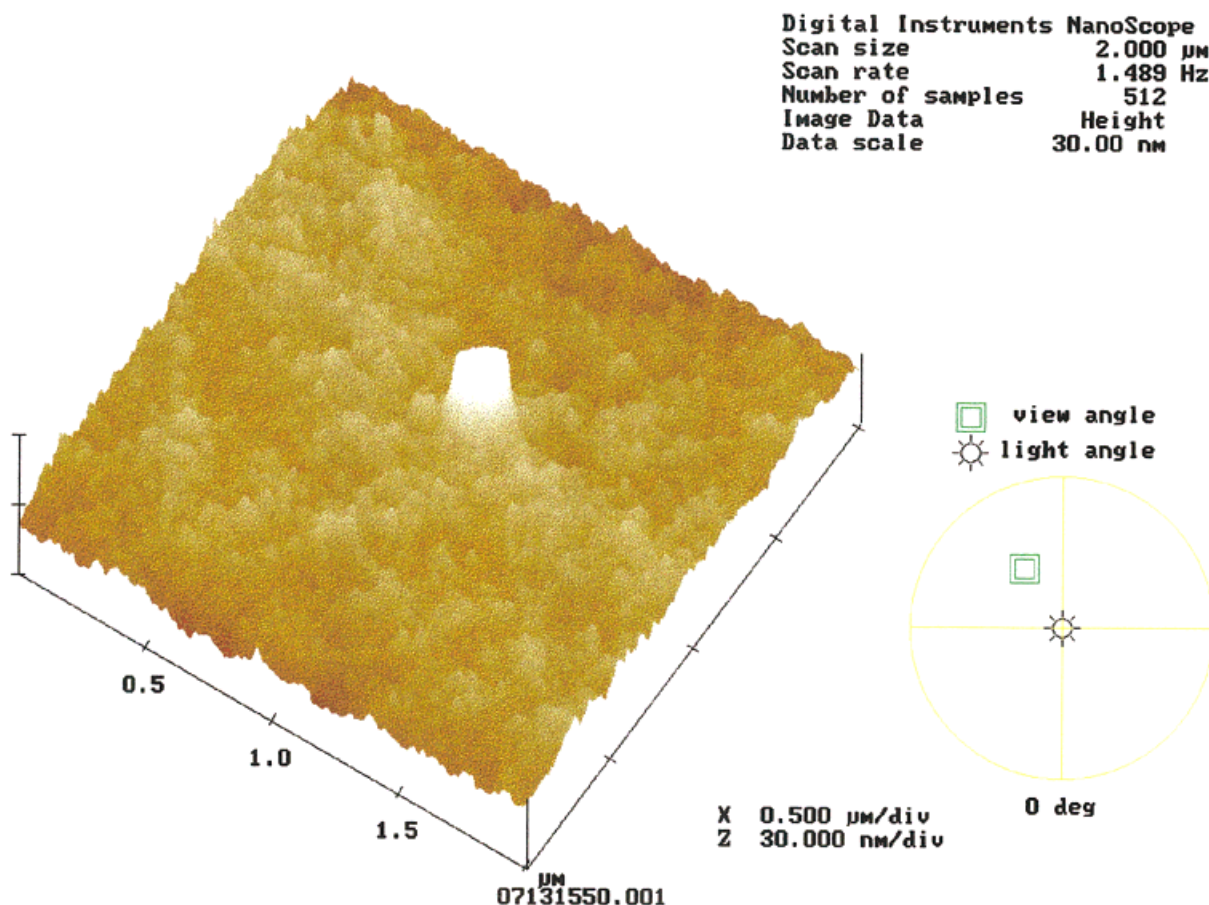


Figure 10 Atomic force micrograph of a Uplex surface treated with concentrated H_2SO_4 for 5 min ($2 \times 2 \mu\text{m}$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

on PI films treated with aqueous KOH are reported in Table V. The experimental data obtained showed an evident variation in the surface chemical composition, in agreement with literature reports.

AFM

AFM was used to investigate the surface topography of PI films, both untreated and those treated with different techniques. Typical pictures obtained are shown in Figures 9–11. It can be clearly seen that the surface contained several almost spherical “bumps” in a surface that was otherwise smooth (roughness $\sim 2 \text{ nm}$). There was no significant change in surface roughness with time of treatment. Untreated film had a surface roughness root mean square of 2.68 nm compared to 1.90 for a surface

treated for 5 min above fuming sulfuric acid and 2.43 for a surface treated for 5 min in concentrated sulfuric acid.

CONCLUSIONS

The purpose of this research work, as clearly stated in the introduction, was to develop chemical procedures for the modification of PIs to improve their adhesion to silver thin layers deposited by sputtering. The results reported in this article clearly demonstrate that this goal was reached in a number of ways and lead to the following general conclusions:

1. Effective chemical procedures based on sulfonation reactions onto PI aromatic

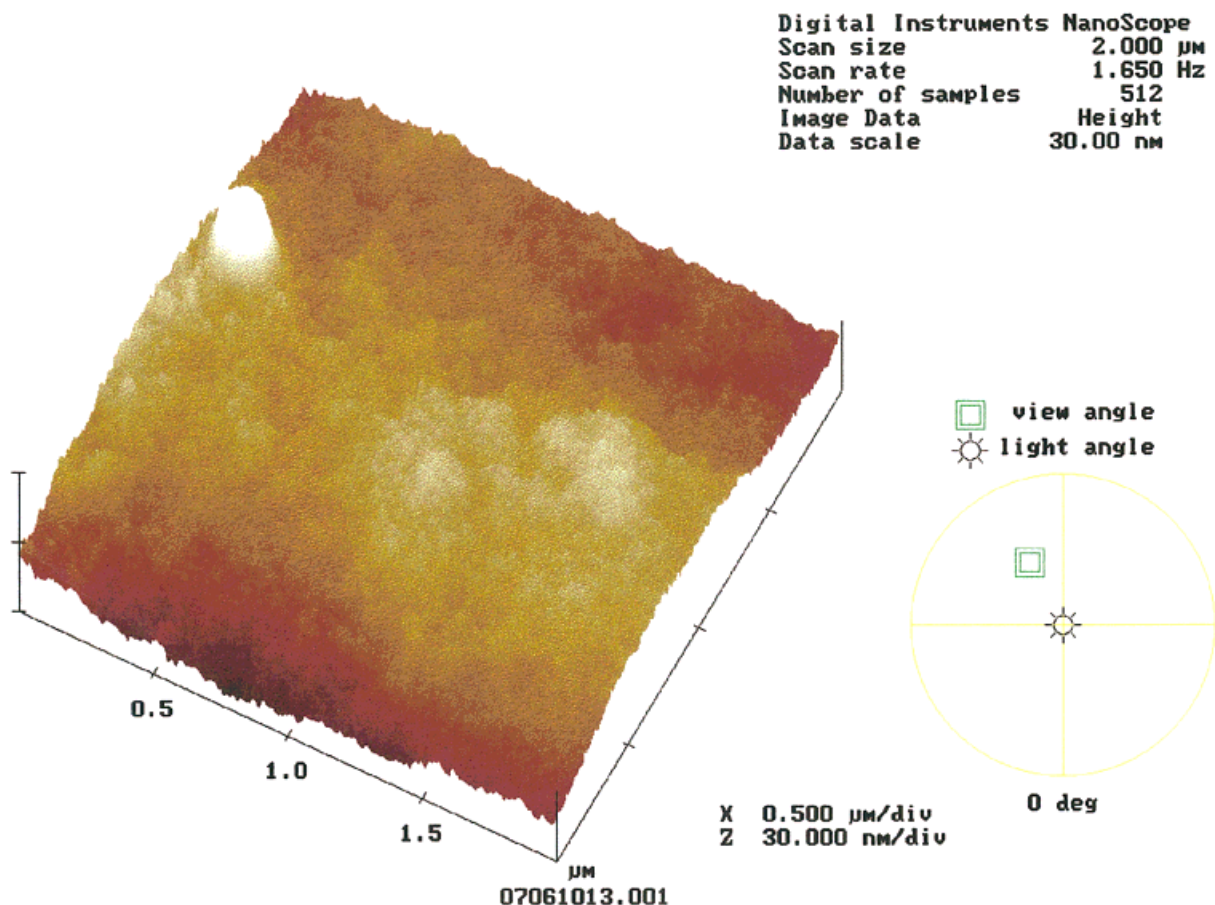


Figure 11 Atomic force micrograph of a Upilex surface treated above fuming H_2SO_4 for 5 min ($2 \times 2 \mu\text{m}$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

rings and etching with KOH aqueous solutions can be used for the surface modification of PIs to increase their adhesion to silver.

- As far as sulfonation reactions are concerned, the most effective experiments, in terms of adhesion performance, turned to be treatments with concentrated sulfuric acid in the presence of silver sulfate as a catalyst and/or gaseous sulfur trioxide. This latter procedure is considered more attractive due its easy execution, the small amount of the active reagent consumed, fast cleaning, and moreover, the possibility to be carried out throughout on line processes.
- Treatments with KOH aqueous solutions at different concentrations and different temperatures proved also to be effective,

but the time required for them to reach the desired adhesion level turned to be higher than for the sulfonation processes. In the case of gas-phase reaction with SO_3 , for instance, contact times as short as 30 s produced optimum PI/silver adhesion.

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