

Immobilization of Surface Active Compounds on Polymer Supports Using Glow Discharge Processes

1. Sodium Dodecyl Sulfate on Poly(propylene)

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A new method has been developed in which a reversibly adsorbed layer of a surfactant (sodium dodecyl sulfate, SDS) is covalently immobilized in one step onto a hydrophobic substrate (poly(propylene), PP) by applying an argon plasma treatment. The adsorption of SDS from aqueous solutions onto PP surfaces was studied with X-ray photoelectron spectroscopy (XPS). Plateau levels of adsorbed SDS were reached within 10 s using SDS solution concentrations above the critical micelle concentration (CMC). At SDS concentrations below the CMC almost no adsorption took place, whereas at SDS concentrations above the CMC constant adsorption levels were measured. Preadsorbed SDS layers could be completely desorbed after immersion of the SDS-coated substrates in water for 90 min. If PP surfaces with preadsorbed SDS were dried and plasma-treated with an argon glow discharge and then immersed in water for 90 min, intact sulfate groups were present at the surface as shown by ion exchange and XPS measurements. This indicates that SDS preadsorbed onto PP surfaces can be immobilized by a plasma treatment. It is concluded that plasma techniques can be used to immobilize physically adsorbed surface active compounds onto substrates. This is a useful way to derivatize inert substrates with various polar or nonpolar groups. © 1993 Academic Press, Inc.

INTRODUCTION

Glow discharge processes have been frequently used to modify material surfaces. Generally two types of processes can be distinguished based on their overall effect on the surface (1-4). Reactive species in the discharge simultaneously etch and deposit onto the surface. Dependent on which effect is dominant, the process is called glow discharge (plasma) treatment (mainly etching) or glow discharge (plasma) polymerization (mainly deposition). Which process occurs is predominantly determined by the gas and plasma conditions used. Generally organic gases and vapors (5-9) form deposits and oxygen and inert gases act as etchants (10-12).

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Although the use of glow discharge processes has many advantages, such as a very shallow modification depth compared to other surface modification techniques, it still has one major drawback. Because the chemical reactions in the discharge itself are rather complex, control and ultimate analysis of the surface chemistry is limited. The chemical structure of the gas or vapor used in the glow discharge process has been thought to play a major role in the surface chemistry. However, the use of amine-containing vapors yielded very different surface concentrations of amine groups in the deposited layer (13, 14). Recent approaches in which a cooled substrate is used have apparently been more successful in obtaining deposited layers with a chemical structure analogous to that of the vapor used (15).

A different approach to modify the surface chemistry of substrates in a controlled way, is to coat substrates with a relatively thick layer—several micrometers—of unsaturated compounds and then treat the precoated substrates with a plasma (16-18). These compounds, which are generally low volatile acrylic monomers, are polymerized and grafted to the substrate by the plasma treatment presumably via free radical reactions. The rate of polymerization and grafting can be enhanced by adding conventional free radical polymerization initiators to the predeposited layer (19, 20). A modification of this concept involves the preswelling of the polymer substrate with an organic solvent followed by exchanging the solvent with an acrylic monomer. The pretreated substrate is then exposed to an inert plasma to graft and polymerize the monomer (21, 22).

From a chemical point of view a glow discharge is a very reactive environment. Different species like radicals, ions, and metastable species are formed and considerable amounts of short wave UV photons are emitted from the plasma (23, 24). Therefore it is doubtful that unsaturated bonds in the predeposited compounds are a necessity for their covalent binding to the substrate. If this is not the case, a more simple and generally applicable process can be developed.

In this study we have tested whether SDS, a saturated alkyl sulfate surfactant can be covalently coupled to a substrate using plasma techniques. PP has been selected as a substrate because the tertiary hydrogen atoms in the backbone are relatively easily abstracted by free radicals. SDS has been selected as an example of a saturated compound, because it can be preadsorbed onto hydrophobic substrates (25–30) and presumably can be desorbed from preadsorbed surfaces which have not been treated with plasma. X-ray photoelectron spectroscopy (XPS) has been used to analyze surfaces in different stages of the immobilization process. SDS gives three distinct XPS signals (oxygen, sulfur, and sodium) compared to the bare PP substrate and this was an additional reason for the selection of SDS as a model compound.

The immobilization process is schematically shown in Fig. 1 and consists of three steps. First, SDS is adsorbed onto the surface and in a second step the preadsorbed surface is plasma-treated. Subsequently a wash step is applied to desorb any unbound SDS. Both the adsorption of SDS onto and the desorption of SDS from PP have been studied using XPS.

After preadsorption of SDS onto PP films (referred to as PP/SDS films), these films are plasma-treated with an argon discharge. Argon has been used because it is relatively inert and it is likely that free radicals will be formed at the surface of the substrate when it is used as a discharge gas. After plasma treatment of the PP/SDS films, films have been washed to remove unbound material. Films have been analyzed with XPS. Different sulfur-containing compounds have also been analyzed with XPS to compare the chemistry of the immobilized SDS with that of known standard samples. In addition ion exchange experiments have been per-

formed to obtain more insight into the chemical structure of immobilized SDS.

MATERIALS AND METHODS

Cleaning of Glassware

Before use all glassware was rinsed three times with toluene (reagent grade, Omni Solv., EM Science, Cherry Hill, NJ 08034), three times with acetone (reagent grade, Omni Solv.), and finally three times with water. In all experiments water was used, which was first deionized and then distilled.

Cleaning and Extraction of the PP Films

PP (Cadillac Plastics, Seattle, WA, thickness 0.5 mm) films were cleaned and extracted to remove stabilizers by treating the films with toluene for 48 h at room temperature. The toluene was changed with fresh solvent two times. The films were dried in a laminar flow hood for at least 4 days.

The extraction of additives and the residual amount of toluene in the PP films was followed by measuring the UV absorbance at different wave lengths. The extraction of (at least) two additives was followed by measuring the absorbance of the film at 230 and 270 nm. The residual amount of toluene was determined by measuring the absorbance at 258 nm. All measurements were done with a Bausch & Lomb Spectronic 1001 spectrophotometer. The absorbance was measured directly by placing the films perpendicular to the UV beam.

From these measurements it was concluded that essentially all additives were removed after extracting the films for 48

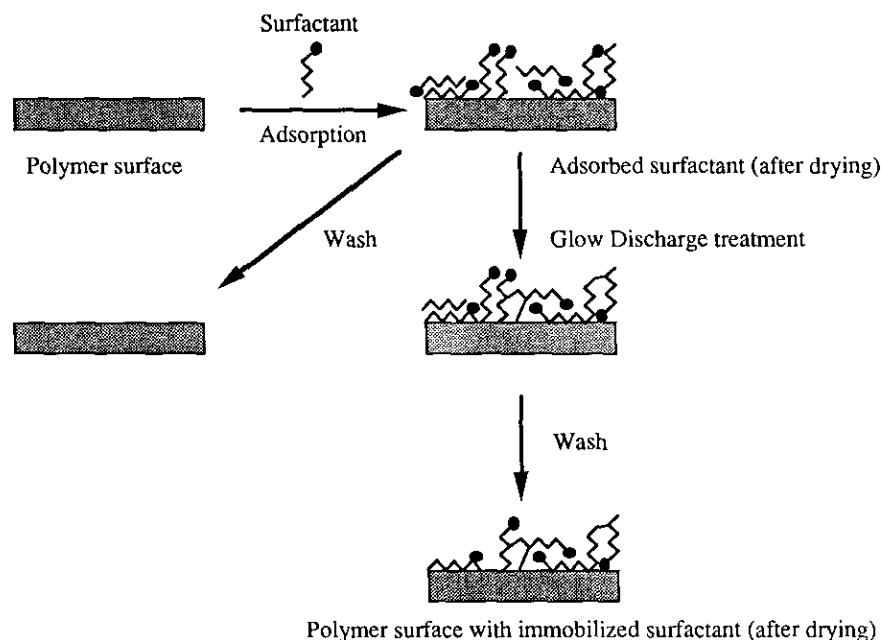


FIG. 1. Schematic diagram of the immobilization of a surface active compound on a substrate by a glow discharge process.

h with toluene. It was also found that all residual toluene could be removed by drying the PP films for at least 4 days in a laminar flow hood.

Adsorption of SDS onto PP Films

It should be noted that the data obtained for the adsorption of SDS on PP do not represent the adsorption under equilibrium conditions. Because the surface analysis of the films is performed in the dry state, the films have to be taken out from the aqueous SDS solution. This implies that the film passes through the solution/air interface, which may influence the adsorption of SDS on the surface.

Toluene-free PP films were dipped into a fresh aqueous solution of SDS (Schwarz/Mann Biotech, Division of ICN Biochemicals, Inc., Cleveland, OH, grade: ultrapure (>99%)) for predetermined times at $25.0 \pm 0.2^\circ\text{C}$. The films were taken out of the solution and dried in vertical position for 16 h in a laminar flow hood. The adsorption of SDS onto PP films was not homogeneous at the bottom part of the films (around 1 cm), because of the remaining droplet on the surface after removal of the film from the solution. For all experiments this part of the surface was discarded. The procedure described above will be further designated as adsorption procedure 1. The amount of SDS adsorbed onto the PP surface was quantified by XPS. A more detailed description is given under Surface Analyses by XPS.

The adsorption of SDS onto PP films was measured as a function of the residence time (10 s–24 h) of the PP film in the SDS solution (24.8 mM). The effect of the SDS solution concentration on the amount of SDS adsorbed was also evaluated. An adsorption time of 30 min and SDS solution concentrations up to 41.4 mM were used.

For some experiments a different adsorption procedure (procedure 2) was used. PP film was extracted with toluene (48 h) and dried for 1 day. These films typically retained 0.8% w/w toluene. They were dipped into a fresh SDS solution in water for 30 min at $25.0 \pm 0.2^\circ\text{C}$. SDS concentrations up to 20.7 mM were used. After taking the film out of the solution, it was dried in a laminar flow hood for 3 additional days to remove all residual toluene.

All PP/SDS films which were to be plasma-treated were preadsorbed with SDS using adsorption procedure 2 (SDS solution concentration 5.79 mM). Only PP/SDS films which were plasma-treated and later used for ion exchange experiments were first preadsorbed with SDS using adsorption procedure 1 (adsorption time 30 min, SDS solution concentration 41.4 mM).

Plasma Treatment of PP and PP/SDS Films

The plasma apparatus used has been described in the literature (31, 4). A Stokes Vane pump (Model 009-2, Pennwalt Corp., Philadelphia, PA) was used to obtain a base pressure of 1.3 Pa. The pressure was measured by a Hastings

thermocouple vacuum gauge (Model VT-6). The films were treated in a large Pyrex tube reactor (80 cm length, internal diameter 11.5 cm). Copper electrodes were placed outside at both ends of the reactor (56 cm separation, capacitively coupled). The radio-frequency power (13.56 MHz) was supplied by an ENI Power Systems generator (Model HF-300, Rochester, NY) and was matched with a matching network to minimize the reflecting power. The argon (Air Products and Chemicals, Inc., Allentown, PA) flow to the reactor was controlled by a mass flow controller (Dyna Mass KM-4).

Films were treated with a static argon plasma (i.e., with no flow through the reactor during the plasma treatment). The treatment procedure was as follows. PP and PP/SDS films were placed in the center region of the reactor. The reactor was evacuated for 15 min. Subsequently an argon flow ($0.5 \text{ cm}^3 \text{ STP/min}$) was established in the reactor and after 2 min the vacuum side was closed. At a pressure of 3.3 Pa the reactor was isolated and subsequently the films were plasma-treated for a predetermined time ranging from 10 s to 600 s. A discharge power of 5 W was used. After the plasma treatment the system was evacuated (to 1.3 Pa) and filled with argon to atmospheric pressure. The films were stored in vials in air at atmospheric pressure.

Plasma-treated PP or PP/SDS films were used either for desorption (washing) and ion-exchange experiments or for XPS measurements.

Desorption (Washing) of PP/SDS Films

PP/SDS films which were either treated or not treated with plasma were immersed in water for 90 min at room temperature. After the films were taken out of the solution, they were dried for 1 day in a laminar flow hood. The films were stored in vials under atmospheric pressure until XPS analysis.

Ion Exchange with Plasma-Treated and Washed PP/SDS Films

PP/SDS films were plasma-treated for different times and washed with water afterwards. After drying they were immersed in an aqueous sodium chloride (1.00 M NaCl) solution for 90 min at room temperature. The films were removed from the NaCl solution and dried for 1 day in a laminar flow hood. The bottom part ($\pm 0.5 \text{ cm}$) of the films on which salt precipitation had taken place was discarded. Surfaces were analyzed with XPS.

Surface Analyses of SDS and Related Compounds

Surfaces of SDS ($\text{C}_{12}\text{SO}_4\text{Na}$) and related compounds (1-dodecane sulfonic acid sodium salt ($\text{C}_{12}\text{SO}_3\text{Na}$) (Sigma Chemical Co., St. Louis, MO 63178), sodium sulfate (Na_2SO_4) (Sigma), sodium sulfite (Na_2SO_3) (Sigma), 1-pentane sulfonic acid sodium salt ($\text{C}_5\text{SO}_3\text{Na}$) (Sigma), lith-

ium dodecyl sulfate ($C_{12}SO_4Li$) (Sigma)) were analyzed with XPS. Samples were obtained by pressing the different powders between aluminum foil with a hydraulic press to form small pellets. These pellets were used for XPS measurements.

Surface Analyses by XPS

The XPS measurements were performed with a SSX-100 spectrometer system (Surface Science Instruments, Mountain View, CA). A detailed description of the experimental procedure is given by Castner *et al.* (32). An $AlK\alpha$ X-ray source with monochromator was used. To minimize charging of polymer samples a 5-eV floodgun was applied. The measurements were performed with a 1 mm diameter spot size. A pass energy of 150 eV was used for survey (0–1000 eV binding energy window) and detail scans (20-eV window). Detail scans were used for quantification. High resolution spectra (20-eV window) were obtained by using a pass energy of 25 eV. A take-off angle (the angle between the surface normal and the axis of the analyzer lens) of 55° was used for all measurements. Only in the depth profile study the take-off angle was varied between 0 and 80° and the angles accepted by the analyzer lens were decreased from 30° to 6° by placing an aperture over the analyzer lens.

After numerical integration of the low resolution detail scans, a calculation of the relative peak areas including considerations of sensitivity factors and number of sweeps was made for the different elements. These relative areas were normalized and an elemental composition in atom percentages was obtained. The whole procedure—integration, calculation and normalization—was performed by software standard to the SSX-100 spectrometer.

The reported binding energies determined from high-resolution spectra are corrected for charging of the sample by setting the CH_x peak maximum in the high resolution C 1s spectra at 284.6 eV.

RESULTS

Adsorption and Desorption of SDS

A XPS survey spectrum of a clean (and extracted) PP film is given in Fig. 2a. A major carbon (C 1s) and a minor oxygen (O 1s) peak can be seen. Fig. 2b shows the survey spectrum of a PP/SDS film. Typical peaks for SDS compared to the bare PP substrate, like sulfur (S 2s and S 2p) and sodium (Na Auger, Na 2s) are found in this spectrum. Also a significant increase of the oxygen (O 1s) peak is found. The corresponding high resolution C 1s spectra of clean PP and of PP/SDS films are given in Fig. 3. The high resolution C 1s spectrum of PP/SDS (Fig. 3b) clearly shows a shoulder on the high binding energy side.

The amount of SDS adsorbed, given in atom percentages, was measured as a function of the residence time of the PP film in the SDS solution. The data plotted in Fig. 4 show that within 10 s a plateau level for sulfur and sodium is

reached. The adsorbed amount does not change significantly if PP surfaces are exposed to the SDS solution for times up to 24 h. Only a slight increase in the amount of oxygen at the surface is found.

Figure 5 shows the amount of SDS adsorbed onto the PP surface as a function of the SDS solution concentration used for adsorption. The critical micelle concentration (CMC, 8.2 mM (30)) is also given in this figure. The adsorption is low at concentrations below the CMC and rises to a constant level at concentrations well above the CMC. At concentrations around the CMC, large standard deviations are found.

Surprisingly the amount of SDS adsorbed onto the surface is apparently enhanced by using PP films with a small residual amount of toluene. The amount of SDS adsorbed on PP films with 0.8% w/w residual toluene, measured as a function of the SDS solution concentration, is given in Fig. 6. A maximum in the amount of SDS adsorbed is found at a solution concentration of 5.79 mM, which is clearly below the CMC. The amount of SDS adsorbed on the surface under these conditions is significantly higher than the amount obtainable with the regular procedure using toluene-free PP.

After immersing PP/SDS films in water for 90 min, the films were dried and survey spectra comparable to Fig. 2a and high resolution C 1s spectra comparable to Fig. 3a were obtained. The specific peaks for SDS have disappeared after washing. Quantitative analysis with detail scans shows that after washing with water, sodium and sulfur can no longer be detected on the surface.

Plasma Treatment of PP/SDS and PP Films

PP/SDS films were plasma-treated with argon for different times and either washed or not washed afterward. Films were subsequently analyzed with XPS. Figure 2c shows a survey spectrum of a plasma-treated PP/SDS film which was washed afterwards. The spectrum clearly shows sulfur peaks, but no sodium peaks could be detected.

In a control experiment, bare PP was plasma-treated with argon under the same conditions as the PP/SDS films. Figure 7 gives the atom percentage oxygen of the surface as a function of the plasma-treatment time. The amount of oxygen rises rapidly and levels out at longer plasma-treatment times.

Figure 7 also shows the atom percentage oxygen of PP/SDS films, which were plasma-treated for different time periods. The amounts of oxygen before and after washing are given. This figure shows that the oxygen level of films which were not washed decreases to a constant level with increasing plasma-treatment time. The oxygen level of washed films increases to a plateau value with increasing plasma-treatment time.

The corresponding sulfur and sodium levels of argon plasma-treated PP/SDS films before and after washing are given in Fig. 8. The sulfur and sodium levels after plasma treatment decrease with increasing plasma-treatment time. A clear maximum in the amount of sulfur on the surface as

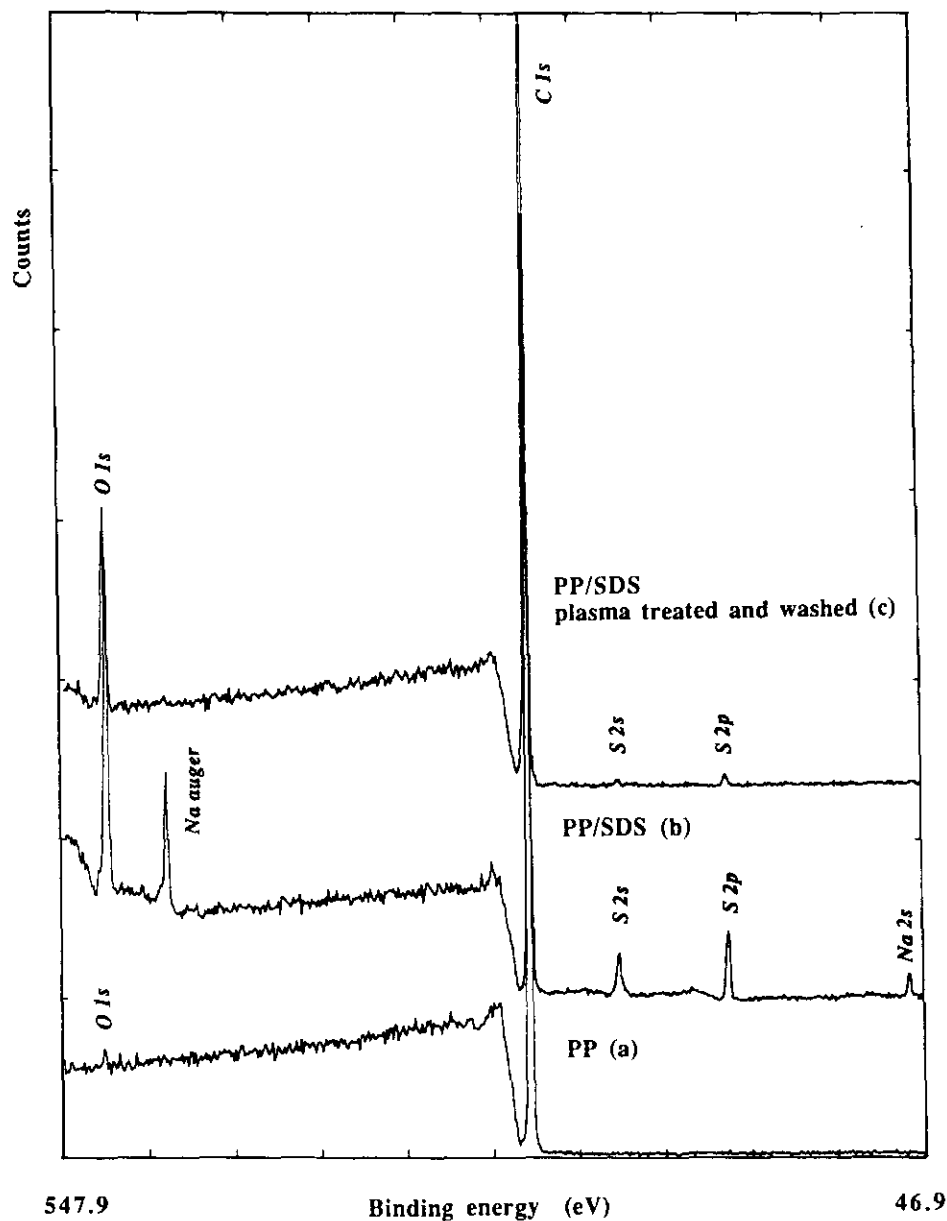


FIG. 2. XPS survey spectra of extracted and cleaned PP (a), of PP/SDS (b), and of PP/SDS which has been plasma-treated for 60 s and washed afterwards (c). Adsorption procedure 1 with an SDS solution concentration of 41.0 mM and an adsorption time of 30 min was used to obtain PP/SDS films.

a function of the plasma-treatment time is found for films which were washed after plasma treatment. At longer plasma-treatment times, starting at around 300 s, the sulfur levels before and after washing are comparable.

After plasma treatment and washing of PP/SDS films, an extra wash step with an aqueous NaCl solution in water was applied. The results of this "ion-exchange" experiment are given in Fig. 9. The sulfur and sodium levels before and after this extra wash step with a NaCl solution are given as a function of the plasma-treatment time. After washing with water no sodium could be detected, but after washing with NaCl solution substantial sodium levels were found. The atom

percentages of sodium and sulfur are equal after the extra wash step for each plasma-treatment time used. Some samples contained small amounts of chlorine, and the sodium levels of these samples were corrected based on the assumption that this chlorine was present as sodium chloride on the surface. If bare PP is plasma-treated, washed, and subsequently immersed in an aqueous NaCl solution no sodium could be detected on the surface.

Table 1 gives the O 1s and S 2p binding energies for the different steps in the immobilization process of SDS onto the PP surface. In this table also the O 1s and S 2p binding energies for pure SDS have been given for comparison.

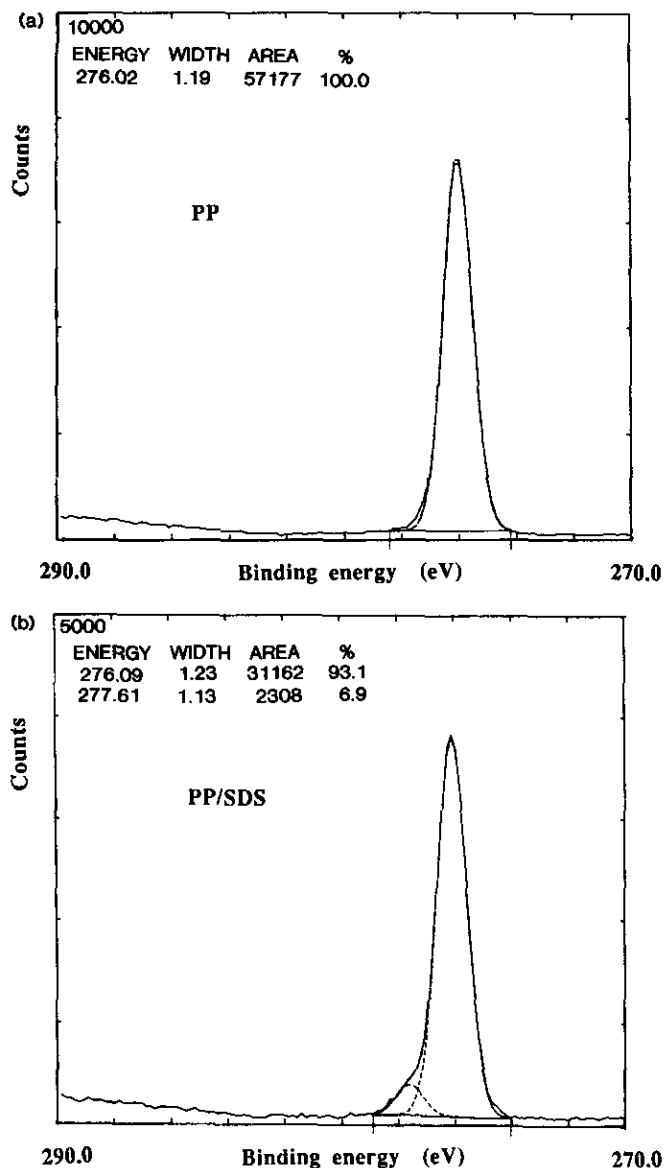


FIG. 3. XPS high resolution C 1s spectra of clean (and extracted) PP (a) and PP/SDS (b). The spectra are given as measured. Adsorption procedure 1 with an SDS solution concentration of 41.0 mM and an adsorption time of 30 min was used to obtain PP/SDS films.

Depth profile studies of films in different stages of the plasma immobilization process were made. In these studies the angle between the XPS analyzer and the sample normal was varied. At glancing angles (take-off angle = 80°) a very small depth is probed and at a take-off angle of 0° the largest depth (around 100 Å) is probed. Figure 10 shows the sulfur levels of PP/SDS and for plasma-treated PP/SDS films with and without washing afterwards. From Fig. 10 it can be seen that for all three cases no significant effect of the take-off angle—and thus of the probed depth—on the amount of sulfur can be found.

The results of the XPS analysis of SDS and related compounds are given in Tables 2 and 3. The elemental com-

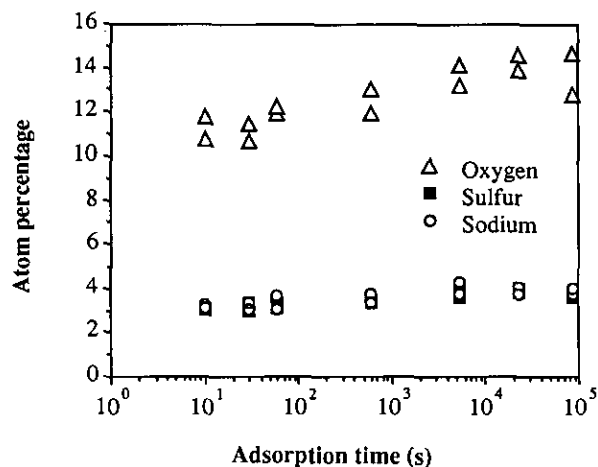


FIG. 4. Adsorption of SDS on PP as a function of the adsorption time. The adsorbed amount of SDS is measured with XPS and is expressed in atom percentages of oxygen, sulfur, and sodium, respectively. An SDS concentration of 24.8 mM was used (duplicate measurements).

positions found and theoretically expected are given in Table 2 and the binding energies (except for the sodium Auger line) are given in Table 3. Some literature values (33) for the binding energies of the O 1s and S 2p peaks for the different sulfur containing groups are also given in this table.

DISCUSSION

Adsorption and Desorption of SDS

Quantitating the adsorption of a surfactant onto a small polymer surface is not a trivial problem. We applied XPS to study the adsorption of SDS on PP. Figure 2 shows that XPS is indeed sensitive enough to be applied to this problem. The main disadvantage of using XPS for surfactant (SDS)

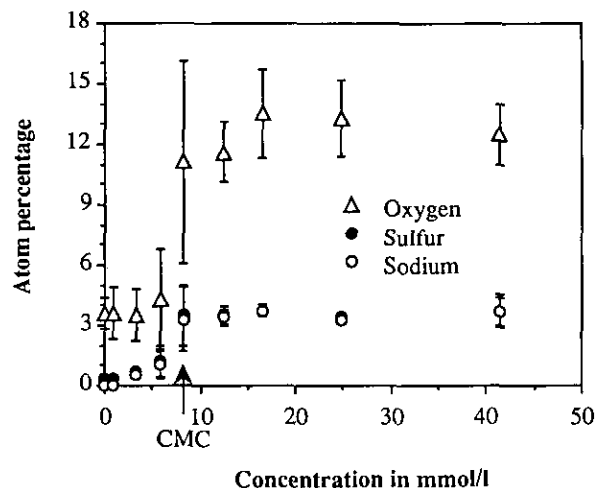


FIG. 5. The adsorption of SDS on PP as a function of the SDS solution concentration as measured with XPS. An adsorption time of 30 min was used (triplicate measurements).

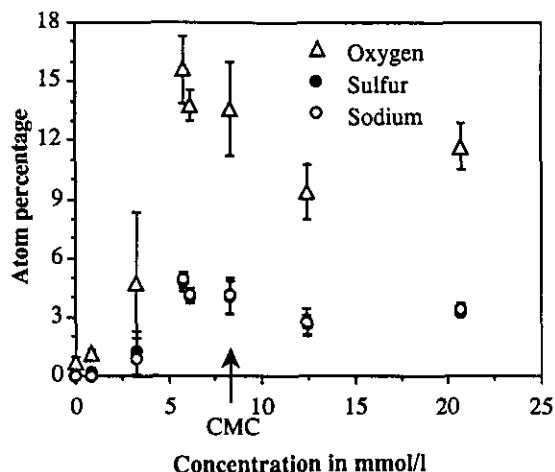


FIG. 6. Adsorption of SDS onto PP which contained residual toluene (0.8% w/w). The relative surface concentration measured with XPS is given as a function of the SDS solution concentration. An adsorption time of 30 min was used (triplicate measurements).

adsorption measurements is that the measurements cannot be performed *in situ*. The samples have to be in a dry state before they can be measured. This implies that after adsorption, the film has to pass the air-aqueous solution interface, which may have an effect on the preadsorbed layer. Furthermore, only relative surface concentrations can be obtained using XPS.

To show that XPS is suitable for the quantification of the adsorption of SDS on PP, XPS was used to analyze the compositions of pure SDS and related compounds. From Table 2 it can be seen that there is a fairly good agreement between the theoretical and measured elemental compositions for $C_{12}SO_4Na$, $C_{12}SO_3Na$, $C_{12}SO_4Li$, and C_5SO_3Na . On Na_2SO_4

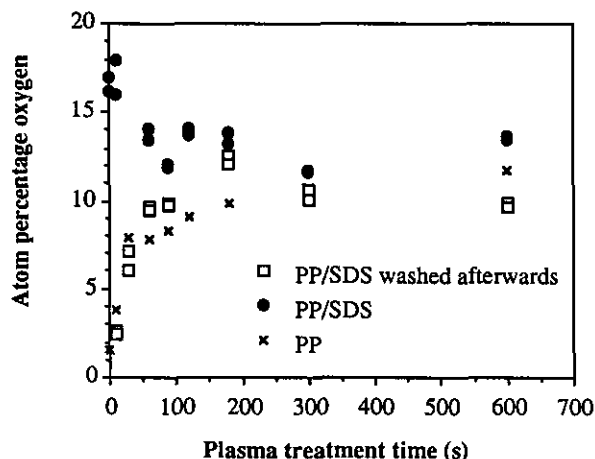


FIG. 7. XPS analysis of plasma-treated PP and PP/SDS films. The atom percentages of oxygen before (for both PP and PP/SDS films) and after washing (for PP/SDS) are given as a function of the plasma-treatment time. Adsorption procedure 2 with an SDS solution concentration of 5.79 mM was used to obtain PP/SDS films. On PP/SDS films duplicate measurements were performed.

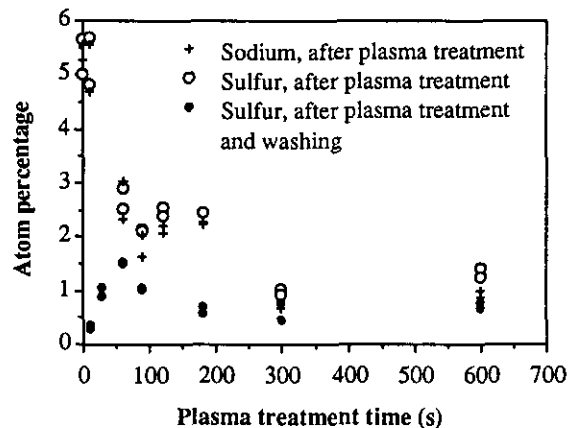


FIG. 8. XPS analysis of plasma-treated PP/SDS films. The atom percentages of sulfur before and after washing are given as a function of the plasma-treatment time (duplicate measurements). Adsorption procedure 2 with an SDS solution concentration of 5.79 mM was used to obtain PP/SDS films.

and Na_2SO_3 some carbon contamination is observed, which can come from many different sources. The measured binding energies given in Table 3 are also in reasonable agreement with the values reported in the literature (33). For $C_{12}SO_3Na$ and C_5SO_3Na C 1s spectra consisting of sharp peaks without shoulders on the high binding energy side (full width at half maximum, FWHM: 1.17 eV) have been found. Based on theoretical calculations (34) a shift of 0.9 eV for the $C-SO_3Na$ carbon group is expected, which has not been observed however.

Figure 2a shows the XPS survey spectrum of a clean PP

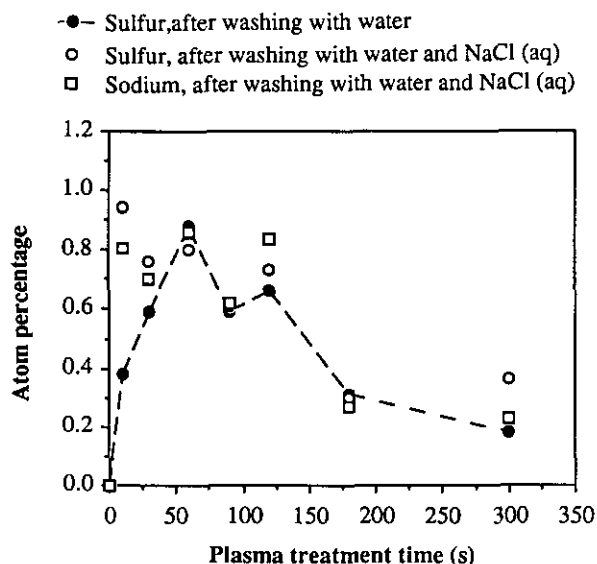


FIG. 9. XPS analysis of PP/SDS films which were plasma-treated and subsequently washed with either water or water and an aqueous sodium chloride solution (1.00 M). The sulfur and corrected sodium levels are given as a function of the plasma-treatment time (see text for details). Adsorption procedure 1 with an SDS solution concentration of 41.0 mM and an adsorption time of 30 min was used to obtain PP/SDS films.

TABLE 1

The Binding Energies for the O 1s and S 2p Peaks for PP and PP/SDS Films in Different Stages of the Immobilization Process

Compound	Binding energy (eV)	
	O 1s	S 2p
Pure SDS	531.8	168.8
PP/SDS	531.8	168.8
PP/SDS plasma-treated and desorbed	532.2 ± 0.1	168.9 ± 0.2
PP plasma-treated	532.7 ± 0.1	

Note. The binding energy of the aliphatic C 1s peak is set on 284.6 eV. The values for pure SDS are also given.

film. In this spectrum, as expected, only carbon and a trace amount of oxygen are seen. The presence of preadsorbed SDS on PP/SDS films can clearly be seen from Fig. 2b. This figure shows an increase in the O 1s peak and the appearance of sulfur and sodium peaks when compared to the bare PP surface.

When the C 1s spectra of PP and PP/SDS films (Figs. 3a and b) are compared, a shoulder on the high binding energy side in the C 1s spectrum of PP/SDS is noted. This shoulder indicates that (at least) a second carbon species is present. When pure SDS is analyzed with XPS a very similar spectrum to that presented in Fig. 3b is found. This indicates that the region probed in the PP/SDS film surface mostly contains SDS. The high resolution C 1s spectrum of SDS consists of two peaks, an aliphatic peak at 284.6 eV (FWHM: 1.18 eV) and a peak due to the C–O–S group at 286.2 eV (FWHM: 1.19 eV). The area ratio of these peaks (C–O–S/C–H = 0.10) is close to the theoretically expected value (0.09).

When the adsorption of SDS (24.8 mM) on PP is measured as a function of time, it can be seen that after 10 s a leveling out in all elemental contents is noted (Fig. 4). At longer adsorption times a small but gradual increase in the oxygen level is seen, which can either be explained by a minor increase in the amount of adsorbed SDS on the surface or by surface oxidation during the adsorption of SDS.

The extent of the adsorption of SDS on PP is probably related to the CMC of SDS. At concentrations below the

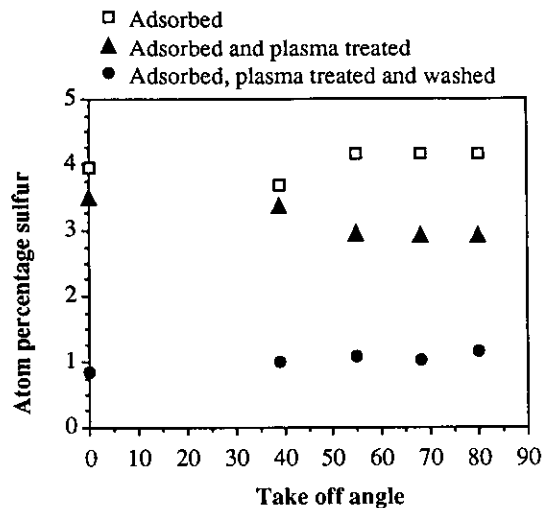


FIG. 10. XPS depth profile measurements of films in different stages of the plasma immobilization process. The sulfur levels are given as a function of the take-off angle used for XPS measurement. Adsorption procedure 2 with an SDS solution concentration of 5.79 mM was used to obtain PP/SDS films. A plasma-treatment time of 60 s was used.

CMC low adsorption levels are observed and at concentrations above the CMC high adsorption levels are found (Fig. 5). A similar relation between the CMC and surface saturation of an anionic surfactant on nonpolar hydrophobic surfaces has been previously proposed by Rosen (30).

When SDS is adsorbed on PP films containing residual toluene, a maximum in the surface concentration of SDS is observed (Fig. 6). Several explanations for the maximum can be given. The residual toluene might be an effective plasticizer. This can cause swelling of the PP surface region and thus decrease the surface crystallinity. Conditions which yield a maximal amount of SDS adsorbed are preferred for the initial plasma-treatment studies of PP/SDS films.

Because the adsorption process—despite its practical simplicity—is very complex on a molecular level, an unambiguous explanation for the observed adsorption behavior in Fig. 5 cannot be given. The polymer film crosses the air-solution interface twice, once before and once after adsorption. The remaining aqueous wetting film on the PP surface after adsorption, which slowly retracts, complicates the pro-

TABLE 2
XPS Analysis of SDS and Related Compounds

Compound	C atom %	O atom %	S atom %	Na atom %	Li atom %
Na ₂ SO ₄	11.6 (0)	46.3 (57.1)	15.0 (14.3)	27.0 (28.6)	
Na ₂ SO ₃	14.8 (0)	40.6 (50.0)	14.6 (16.7)	30.0 (33.3)	
C ₅ SO ₃ Na	49.0 (50.0)	27.4 (30.0)	11.7 (10.0)	11.9 (10.0)	
C ₁₂ SO ₃ Na	71.2 (70.6)	14.9 (17.6)	7.0 (5.9)	6.8 (5.9)	
C ₁₂ SO ₄ Na	68.6 (66.7)	18.3 (22.2)	6.7 (5.6)	6.5 (5.6)	
C ₁₂ SO ₄ Li	67.7 (66.7)	17.6 (22.2)	6.5 (5.6)		6.5 (5.6)

Note. The measured elemental compositions are compared to the theoretically expected compositions (in parentheses).

TABLE 3
The Binding Energies for the O 1s and S 2p Peaks for SDS
and Related Compounds

Compound	Oxygen (eV)	Sulfur (eV)
Na ₂ SO ₄	531.0 (531.7–531.9)	168.2 (168.4–168.6)
Na ₂ SO ₃	530.5 (531.4–531.6)	166.4 (166.2–166.4)
C ₅ SO ₃ Na	531.0 (531.7–532.0)	167.7 (167.9–168.1) ^a
C ₁₂ SO ₃ Na	531.2 (531.7–532.0)	167.8 (167.9–168.1) ^a
C ₁₂ SO ₄ Na	531.8	168.8
C ₁₂ SO ₄ Li	532.2	169.1

Note. The binding energy of the aliphatic C 1s peak is set on 284.6 eV. Some literature values (33) are given in parentheses for comparison.

^a Value given for Phenyl-SO₃Na.

cess even more. At concentrations below the CMC no aqueous film was observed on the surface after adsorption. This is probably caused by the fact that at low SDS concentrations the surface tension of the SDS solution is not sufficiently reduced to permit spreading on the PP surface.

Although no definite statement can be made about the exact arrangement of SDS molecules on the PP surface after adsorption, we expect a kind of monolayer of SDS to be adsorbed on a PP substrate at concentrations above the CMC. The thickness of this layer should be less than the probe depth of XPS. Thus, if an XPS depth profile study is made, the sulfur level is expected to increase with increasing (more glancing) angle. From Fig. 10 it can be seen that the sulfur content is independent of the take-off angle, which indicates that the sulfur is homogeneously distributed throughout the probed depth. Figure 10 shows the data for a PP/SDS film which was preadsorbed according to procedure 2—with some residual toluene left before adsorption—, but when dry PP is used for adsorption a similar trend is found. The observed behavior is in conflict with the expected model. It is not clear whether the postulated homogeneous layer is caused by the adsorption and penetration of SDS into the depth of the PP surface regions, or if SDS mixing and distribution within the surface layer takes place during vacuum drying and/or XPS measurements. Holmes-Farley *et al.* (35) have shown that surface reconstruction (homogenization) can occur for oxidized PE and PP upon heating under vacuum.

When PP/SDS films are immersed in water for 90 min and analyzed with XPS, no sulfur or sodium could be detected on the surface. These desorption conditions are thus sufficient to remove all adsorbed SDS from the PP surface, regardless of the concentrations or conditions used for adsorption.

Plasma Treatment of PP/SDS and PP Films

Plasma treatment of PP films has been performed as a control for the plasma-treated PP/SDS films. Although the general effects of treating a polymer with an argon plasma are known (1, 10, 36), this control is still needed to define specific effects of the plasma conditions used. When PP (or

any other polymer) is plasma-treated with argon, etching of the surface can occur, and if an oxygen source—like adsorbed water or air leakage—is present, oxidation of the surface also takes place. These processes occur simultaneously and are cooperative. The argon plasma also introduces free radicals on the surface which could react with oxygen if the film is exposed to air after the plasma treatment. From Fig. 7 it can be seen that some of these processes could indeed be occurring when PP is plasma-treated with argon. After an initial rapid rise, the oxygen content levels out at longer plasma-treatment times, which indicates that a steady state between the etching and oxidation processes is being approached.

When PP/SDS films are plasma-treated with argon, oxidation and etching of the surface should also occur as they did for the PP control. This can be seen in Fig. 7. For the films which are not washed after the plasma treatment, the amount of oxygen initially decreases due to etching of the oxygen-rich sulfate groups of the preadsorbed SDS molecules at the surface. At longer times the amount of oxygen levels out, probably because a steady state is reached. Also from Fig. 8 it can be seen that, due to the etching process, the amounts of sulfur and sodium decrease with increasing plasma-treatment time for PP/SDS films which have not been washed after the treatment.

The presence of sulfur on plasma-treated PP/SDS films which have been washed clearly shows that SDS is immobilized onto the PP surface by the plasma treatment. The maximum in the amount of sulfur on the surface as a function of the plasma-treatment time for washed, plasma-treated PP/SDS films (see Fig. 8) can be explained by the simultaneous action of the plasma immobilization and etching process. The oxygen incorporated on the surface of washed, plasma-treated PP/SDS films (in Fig. 7) is thus due to the simultaneous action of at least two processes, immobilization and oxidation. This explains why the amounts of oxygen on plasma-treated and washed PP/SDS films at plasma-treatment times between 60 and 200 s appear to be slightly higher than those for plasma-treated PP surfaces.

After washing of plasma-treated PP/SDS films, no sodium is found on the surface. The sodium counterions on the surface must have been exchanged for hydronium ions since the sulfate groups are essentially unchanged (see below). Drummond and Grieser (37) reported that the ion exchange constant of H⁺ for Na⁺ ions in SDS micelles is 1.3 ± 0.4 . Thus in a sodium-deficient medium all the sodium counterions should be exchanged for hydronium ions.

Figure 9 shows that for plasma-immobilized SDS, ion exchange indeed occurs if an extra wash step with 1 M NaCl is applied. The data show that all sulfur-containing groups immobilized on the surface are capable of undergoing ion exchange regardless of the plasma treatment time. This indicates that all sulfur groups have a charge of -1 , and that this charge is not affected by the plasma treatment.

Based on the binding energy of the S 2p peak of plasma-treated PP/SDS surfaces after washing, some additional in-

formation on the chemical state of the immobilized SDS molecules can be obtained. The binding energies of the S 2*p* and O 1*s* peaks in the different stages in the immobilization process are given in Table 1. The binding energy of the S 2*p* peak does not change during the immobilization process and is similar to the binding energy of the S 2*p* peak of pure SDS. If the sulfate groups would have been modified by the plasma treatment to, e.g., sulfonate groups, a shift in the S 2*p* binding energy should have been observed (see Table 3). These data strongly suggest that the sulfate group of preadsorbed SDS is not chemically modified by the plasma treatment. The ion exchange properties of the surface-bound sulfate groups support this conclusion.

The binding energy of the O 1*s* peak of plasma-treated PP/SDS films which were washed afterwards is slightly higher than the binding energy of the O 1*s* peak for pure SDS. The binding energy of the O 1*s* peak of plasma-treated PP is still higher. Because the oxygen on plasma-treated and washed PP/SDS films is due both to immobilization of sulfate groups and oxidation, the binding energy of the O 1*s* peak should be shifted slightly upwards.

The depth-profiling study given in Fig. 10 shows that the adsorbed SDS layer, which is apparently uniformly distributed in the top 100 Å (according to the XPS measurements), remains homogeneous throughout the immobilization process.

These results show that it is possible to immobilize preadsorbed SDS on PP by an argon plasma treatment. It is not possible to directly couple SDS onto PP by conventional chemical means, because of the lack of functional groups both on the substrate and SDS. This shows the potency of this simple two-step immobilization method.

The immobilization efficiency of SDS is still low. A yield of 25% is indicated, based on the amounts of sulfur after adsorption and after immobilization and washing. Probably this efficiency can be increased by optimizing the process conditions. In this study only the effect of the plasma-treatment time has been investigated. Several other parameters such as discharge power, pressure, substrate temperature, and gas/vapor used can be optimized to increase the immobilization efficiency.

The chemical state of the immobilized SDS has only been partially elucidated. Direct XPS analysis and ion exchange experiments show that the sulfate group of SDS immobilized on the PP surface is still present after the argon plasma treatment. On the other hand hardly any information on the chemical state of the immobilized alkyl tail of SDS could be obtained. Although some additional oxygen was incorporated on the PP/SDS surface by the plasma treatment, it is not possible to assign such oxidation states specific to the SDS alkyl tail or to the PP substrate. Also it is difficult to determine if the treatment causes the SDS alkyl tail to be branched, shortened, or to form unsaturated bonds. Static secondary ion mass spectroscopy (SSIMS) may give some answers in this respect.

The mechanism by which the plasma treatment immobilizes the adsorbed SDS is still unclear. There are two key questions to be answered in elucidating the mechanism: which species in the plasma are responsible for the immobilization and what is the exact mechanism by which SDS is bound to the surface.

From a chemical point of view a glow discharge is a harsh environment. Several reactive species in the glow discharge have sufficient energy to cleave (and form) any chemical bond. Not only chemically reactive species like radicals and ions but also free electrons with a kinetic energy distribution between 2–8 eV are observed in glow discharges (3). Moreover, short wave UV photons (23, 24) with wavelengths as low as 100 nm (with an energy equivalent to 12 eV) complicate the plasma chemistry even more. For comparison a typical chemical bond has an energy of 3–4 eV.

Different mechanisms for the immobilization of the SDS alkyl tail to the polymer substrate seem possible. The plasma can create radicals both on the alkyl tails and on the polymer chains of the substrate and recombination of these radicals can give covalent coupling of SDS to the substrate. Also by hydrogen abstraction, unsaturated bonds can be generated (38) on either the SDS alkyl tail or on polymer chains of the substrate (or on both). These unsaturated bonds can be opened by radicals and covalent coupling can occur. Although a radical mechanism seems most likely to be responsible for the immobilization, the mechanism still needs to be carefully elucidated. Further study of the chemical state of the alkyl chain of immobilized SDS on PP will be helpful in this respect.

CONCLUSIONS

By conventional chemical means it is often not possible to directly couple a preadsorbed saturated compound onto a hydrophobic substrate. Therefore a new method has been developed in which a (reversibly) adsorbed layer of a surfactant (SDS) can be irreversibly immobilized in one step onto a hydrophobic substrate (PP) by applying an argon plasma treatment to the preadsorbed layer on the substrate.

Additionally it was shown in this study that the adsorption of SDS from aqueous solutions on PP can be measured conveniently with XPS. When PP surfaces are exposed to an aqueous SDS solution with a concentration well above the CMC, plateau levels of adsorbed SDS are reached within 10 s. At SDS solution concentrations below the CMC almost no adsorption takes place. SDS adsorbed onto PP can be desorbed by immersing PP/SDS films in water for 90 min.

When PP preadsorbed with SDS is treated with a low power, low pressure, argon glow discharge followed by washing, surfaces with significant retained sulfur levels were obtained. Thus the adsorbed SDS is partially immobilized on the PP surface by the glow discharge treatment. Based on the ion exchange properties of immobilized SDS plus the binding energy of the S 2*p* peak as analyzed with XPS anal-

ysis, it was concluded that the sulfate groups are still intact after immobilization on the PP surface. Therefore immobilization of SDS probably takes place via crosslinking of the SDS alkyl tail. Although the exact chemistry involved in this immobilization process is not clear, this method seems to be a useful way of irreversibly immobilizing reactive or functional groups to a surface.

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