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Introduction of sulfate groups on poly(ethylene) surfaces by argon plasma immobilization of sodium alkyl sulfates

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Sulfate groups were introduced at the surface of poly(ethylene) (PE) samples. This was accomplished by immobilizing a precoated layer of either sodium 10-undecene sulfate (S11(:)) or sodium dodecane sulfate (SDS) on the polymeric surface by means of an argon plasma treatment. For this purpose, S11(:) was synthesized by sulfating 10-undecene-1-ol using the pyridine-SO_3 complex. The presence of sulfate groups at the polymeric surfaces was confirmed by X-ray Photoelectron Spectroscopy (XPS). The presence of an unsaturated bond in the alkyl chain of the surfactant improved the efficiency of the immobilization process. About 25% of the initial amount of sulfate groups in the precoated S11(:) layer was retained at the PE surface compared to only 6% for SDS. The maximum surface density of sulfate groups on the resulting samples was one group per 45 and 127 Å^2 respectively. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: surface modification; sulfation; argon plasma treatment)

INTRODUCTION

Sulfur containing ionizable groups have been introduced at polymeric surfaces to improve their performance in biomedical[1–5] and electrical[6–9] applications. In biomedical research these groups are used to improve the blood and cell compatibility of polymeric surfaces.

There are two approaches to obtain polymers with sulfur containing ionizable groups at their surface. First, new polymers with sulfur containing groups may be synthesized[5,10–14]. Although part of the functional groups may be present at the surface of devices processed from these newly synthesized polymers, there are some drawbacks to this approach. This approach is restricted to specific types of polymers, the concentration of sulfur containing functional groups at the surface is usually low, and the mechanical properties of the polymers may be poor especially when the polymers are in a hydrated state[15]. Therefore a second approach, by which the outermost surface of existing polymers is modified leaving the bulk properties unaltered, is more widely applied.

Surface modifications have been performed by using solution or gas phase reaction media. Immersing poly(ethylene) (PE) or poly(styrene) (PS) samples in pure or in fuming sulfuric acid resulted in the introduction of sulfonic acid groups at these surfaces[1,16–18]. Except for sulfate groups also other oxygen containing groups were introduced at the PE surface using concentrated sulfuric acid containing $KMnO_4$[19,20]. The modifications were generally not restricted to the outermost surface but are reported to extend over several micrometers in depth. Chlorosulfonic acid proved to be a powerful sulfonating reagent for PS but the physical integrity of PS samples was lost[18]. By using

dilutions, PS surfaces could be chlorosulfonated after which the chlorosulfonate groups were hydrolyzed into sulfonate groups[21,22]. The reaction of chlorosulfonic acid with PE is very slow. Therefore it seems that this method is only applicable to certain types of polymers.

The sulfonation of polymers with gaseous SO_3 has the advantage that the modification is limited to the depth of only a few nanometers and that unwanted processes such as oxidation and degradation induced by solvents are eliminated. A disadvantage is that this method is limited to phenyl group containing polymers[6,23].

Gas plasmas have also been used to introduce sulfur containing functional groups at polymeric surfaces. Plasma polymerization of monomer/SO_2 mixtures[7–9] and treatment of polymers with SO_2 plasmas have been reported[2,3,24,25]. Due to the complexity of the plasma phase, the surface chemistry cannot be controlled as well as desired. It was therefore not possible to selectively introduce one particular functional group. Usually, a wide variety of sulfur containing groups such as thio, sulfone, sulfinic acid, and sulfonic acid groups were introduced. The specificity towards one particular functional group can be increased by pretreating polymeric surfaces with an ammonia plasma thereby introducing radicals and amino groups at the surface[4,25]. In one study SO_2 was flushed through the reactor, which reacted with the radicals at the surfaces before exposure to air[25]. In another study the polymeric substrates were removed from the reactor and the amino groups were reacted with λ-1,3-propane sultone[4]. Due to the carcinogenic nature of this reagent, its use should be avoided.

With a previously developed plasma treatment method, called plasma immobilization, it was possible to specifically introduce sulfate groups without introducing other sulfur containing functional groups at a poly(propylene) (PP) surface[26]. For this purpose, sodium dodecane sulfate (SDS)

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was coated onto PP samples. When the precoated samples were immersed in water, all of the precoated SDS was removed. However, when the precoated samples were treated with an argon plasma, part of the SDS layer could not be removed by washing with water but was covalently immobilized on the surface. X-ray Photoelectron Spectroscopy (XPS) analysis showed that the sulfate groups were not chemically modified by the plasma treatment.

The general aim of our studies is to improve the blood compatibility of polymers by introducing specific functional groups at their surfaces. Among others, the effect of sulfate groups at polymeric surfaces on the blood compatibility will be investigated. The surface modification method that will be used should preferably be applicable to a wide variety of polymers in different geometries. The modifications should be restricted to the surface thus without affecting the bulk properties of the substrates. Consequently, the plasma immobilization method seems very suitable for this purpose.

In this paper, the applicability of this method for the introduction of sulfate groups at PE surfaces is investigated. PE was chosen as a model substrate, because due to its chemical structure, surface modifications can easily be evaluated with XPS. Recently, carboxylate group containing surfactants were immobilized on PE via this method[27]. The presence of an unsaturated bond in the alkyl chain improved the efficiency of the immobilization process. Therefore not only the immobilization of SDS on PE but also the immobilization of sodium 10-undecene sulfate (S11(:)) on PE was investigated. This surfactant was obtained by sulfating 10-undecene-1-ol (C11(:)OH).

EXPERIMENTAL

Materials

PE foil without additives (LDPE, type 2300, thickness 0.2 mm) was obtained from DSM (Geleen, The Netherlands). Argon (purity $\geq$ 99.999%) was purchased from Hoekloos (Schiedam, The Netherlands). 10-Undecene-1-ol (C11(:)OH) was purchased from Aldrich (Milwaukee, U.S.A.). 1,3-didecyl-2-methyl-imidazolium chloride (DDMICl) was purchased from Metrohm (Herisau, Switzerland). All other chemicals were purchased from Merck (Darmstadt, Germany). The solvents that were used were all of analytical grade quality. Pyridine was distilled in the presence of tosylchloride prior to use. Other chemicals were used as received.

Cleaning of glassware

All glassware was cleaned by rinsing three times with toluene, three times with acetone, three times with deionized water, and finally three times with acetone and then dried.

Cleaning of PE samples

PE samples (13 × 25 mm) were ultrasonically cleaned (ten minutes, four times in each liquid) successively in dichloromethane, acetone, and deionized water and then dried at room temperature (RT) *in vacuo*.

Analyses of surfactants

*FT*i.r.-spectra were recorded using a Biorad FTS-60 spectrometer (16 scans, res. 4 cm^{-1}). ^{1}H-n.m.r.-spectra were recorded using DMSO-d$_6$ and a Bruker AC-250 F spectrometer. Elemental analyses were carried out by the

Laboratory of Chemical Analysis of the University of Twente. The amount of sulfate groups was determined by a potentiometric titration with DDMICl. A high-sense surfactant electrode and a Ag/AgCl electrode (both Metrohm, Herisau, Switzerland) were used as working and reference electrode respectively.

The critical micelle concentration (cmc) of surfactant was determined by measuring the surface tension and the conductivity of aqueous surfactant solutions of different concentrations. Surface tensions were measured with the Wilhelmy plate technique using a platinum plate and a Processor Tensiometer K12 (Krüss GmbH, Hamburg, Germany). The conductivity was determined using a PW9526 Digital Conductivity Meter (Philips, Eindhoven, The Netherlands) and a platinized electrode with a current source of approximately 25 mA. All measurements were performed at RT.

Synthesis of sodium 10-undecene sulfate (S11(:))

Alcohols can be sulfated with the pyridine-SO$_3$ complex at moderate temperatures in the presence of an excess of pyridine. The pyridine-SO$_3$ complex was synthesized according to Dolars[28]. In a typical experiment, pyridine (60 ml, 0.74 mole) and chloroform (100 ml) were mixed and cooled to 2°C. Under vigorous stirring, chlorosulfonic acid (20 ml, 0.30 mole) was slowly added over a period of 1.5 h. Upon addition a precipitate was formed. During reaction the temperature was kept below 10°C. After stirring for another half hour, the white precipitate was filtered and extensively washed with chloroform. The product was dried *in vacuo* at 40°C. Yield 29.8 g (0.19 mole, 62% based on the initial amount of chlorosulfonic acid).

C11(:)OH was sulfated according to a method as described by Maaskant[29]. A mixture of the pyridine-SO$_3$ complex (56 g, 0.35 mole) in 100 ml of pyridine was heated to 105°C. The complex melted yielding a slightly yellow coloured mixture. C11(:)OH (30 g, 0.18 mole) dissolved in 150 ml of pyridine was added to the mixture and the reaction mixture was stirred at 105°C for 2.5 h. During the reaction the yellow colour of the mixture darkened and became brown. Subsequently, the mixture was cooled to RT. Ice cooled water (100 ml) was added and the pH of the reaction mixture was raised from 3 to 11 by adding an aqueous solution of 5 M NaOH. The resulting solution was concentrated to 150 ml using a rotavapour and slowly added to 400 ml of acetone. A white precipitate, which was analysed and identified as Na$_2$SO$_4$, was removed by filtration (glass filter por. 5). The solvent was removed from the filtrate using a rotavapor. The slightly yellow residue was purified by recrystallization twice from ethanol yielding 39.5 g of S11(:) (0.15 mole, 82% conversion based on the initial amount of C11(:)OH).

^{1}H-n.m.r. (DMSO-d$_6$): d = 5.80 (m, 1H, CH$_2$=C*H*), 4.95 (m, 2H, C*H$_2$*=CH), 3.70 (t, J = 6.8 Hz, 2H, C*H$_2$*OSO$_3$Na), 2.02 (q, J = 6.8 Hz, 2H, CH$_2$=CHC*H$_2$*), 1.49 (m, 2H, C*H$_2$*CH$_2$OSO$_3$Na), 1.25 (m, 12H, C*H$_2$*).

*FT*i.r. (KBr): 1251, 1204 cm^{-1} (ν_{as}(SO$_4^-$)), 1081 cm^{-1} (ν_{sy}(SO$_4^-$)).

Anal. C$_{11}$H$_{21}$SO$_4$Na: C, 48.5; H, 7.8; S, 11.8; Na, 8.4; SO$_4^-$, 3.67 meq/g (calculated). C, 48.4 ± 0.1; H, 7.7 ± 0.1; S, 11.7 ± 0.1; Na, 8.1 ± 0.2; SO$_4^-$, 3.70 ± 0.03 meq/g (analysed).

Coating of S11(:) and SDS onto PE

Clean PE samples were placed in test tubes and aqueous solutions of 0.20 M (unless otherwise mentioned) S11(:) or

SDS containing 1 vol.% of hexanol were added. After 15 min, the solutions were removed from the test tubes and the polymeric samples were dried at RT *in vacuo*. The resulting samples are coded as PE/S11(:) and PE/SDS respectively.

Plasma treatment of PE and precoated PE samples

The plasma treatments were performed in a tubular reactor (length 80 cm, internal diameter 6.5 cm) using three capacitively coupled externally placed electrodes. The hot electrode was placed at the center of the reactor and the cold electrodes were placed at 10 cm distance at both sides of the hot electrode. The electrodes were connected to a RF (13.56 MHz) generator through a matching network. The vacuum side of the reactor was connected to a two stage rotary pump and a turbomolecular pump. The gas flow to the reactor was controlled by mass flow controllers. The PE and precoated PE samples were placed on glass plates that were put in the centre of the reactor between the electrodes. The reactor was evacuated to a pressure of 1×10^{-5} mbar (1 bar $= 10^5$ Pa) and flushed four times with argon after which an argon flow of 10 cm^3/min (STP) was established through the reactor. After 15 min, the samples were treated with a static argon plasma, i.e. with no flow through the reactor during the plasma treatment (45 W, 0.07 mbar). After the plasma treatment, the argon flow was established through the reactor again for 2 min. Subsequently, the reactor was brought to atmospheric pressure with argon. The samples were removed from the reactor, turned, and the other side of the samples was plasma treated according to the same procedure.

Washing of polymeric samples

Polymeric samples were immersed in an aqueous solution of 0.1 mM HCl for 1 h at RT, rinsed twice with 0.1 mM HCl, and dried at RT *in vacuo*.

X-ray photoelectron spectroscopy (XPS)

A Kratos XSAM-800 apparatus equipped with a Mg-K_a X-ray source (15 kV, 10 mA) was used to analyse the surface composition of polymeric samples. The analyser was placed perpendicular to the sample surface. Survey scans (0–1100 eV) and detail scans were recorded at an analyser pass energy of 40 eV (FWHM Ag $3d^{5/2}$: 1.2 eV) and an X-ray spot size with a diameter of 3 mm. Survey scans were used to qualitatively determine the elemental composition of the samples. No charge neutralization was applied and the reported values of the binding energies were referenced to the C 1 s peak for aliphatic carbon which was assigned a value of 284.8 eV[30]. The relative peak areas for the different elements were calculated by numerical integration of the detail scans, considering empirically derived sensitivity factors. After normalization, an elemental composition in atomic percentages was obtained. All calculations were performed using the multi-user DS 800 software system (Kratos, Manchester, England).

Contact angle determinations

Advancing and receding contact angles were determined using the Wilhelmy plate technique with the aid of an Electrobalance, Model RM-2, Cahn/Ventron (Paramount, CA, U.S.A.)[31]. The interfacial velocity was 4 mm/min.

RESULTS AND DISCUSSION

Sulfation of C11(:)OH

Since no sulfate containing unsaturated surfactant was commercially available, it was synthesized from its corresponding alcohol. Alcohols can be sulfated with SO_3 or sulfuric acid. However, these reactions are difficult to perform and the harsh conditions result in side reactions. Chlorosulfonic acid cannot be used for the sulfation of unsaturated alcohols because it attacks double bonds[32]. Complexes of amines and SO_3 are very mild reagents and the pyridine-SO_3 complex is used to sulfate carbohydrates, sterols, alkenols, and other sensitive compounds[33–35]. Therefore this complex was used to sulfate C11(:)OH.

The sulfation of C11(:)OH with the pyridine-SO_3 complex was successful and the product S11(:) was pure according to the results of the elemental analyses and sulfate group titration. This was supported by the results of FTi.r. and ^{1}H-n.m.r. measurements. The characteristic peaks of the alcohol were not observed anymore in the FTi.r. spectrum of S11(:). New peaks at 1251, 1204 ($\nu_{as}(SO_4^-)$), and 1081 cm^{-1} ($\nu_{sy}(SO_4^-)$) could be detected indicating the conversion of the alcohol into a sulfate group. In the ^{1}H-n.m.r. spectrum of S11(:) the chemical shift of the proton of the OH group at 4.34 ppm was not observed. Furthermore, the α-CH$_2$ protons were shifted from 3.35 to 3.70 ppm and a shift of the β-CH$_2$ protons from 1.38 to 1.49 ppm was observed. From n.m.r. analysis of SDS it is known that the α-CH$_2$ protons shift to 3.70 ppm.

The peaks in the FTi.r. spectra at 3077 cm^{-1} (ν(CHR$_1$=CH$_2$)) and 1644 cm^{-1} (ν(C=C)) were not decreased after reaction. This indicates that no modification of the double bond had occurred. This was confirmed by ^{1}H-n.m.r. spectroscopy. From the relative integrals no decrease in the amount of protons of the CH$_2$ and CH group of the double bond at chemical shifts of respectively 4.95 and 5.80 ppm were observed and therefore it is concluded that the double bond remains unaltered during sulfation.

Recrystallization of S11(:) from ethanol was necessary because the crude material still contained small amounts of an impurity, probably C11(:)OH. Although no chemical shift of the OH proton at 4.35 ppm was observed in the ^{1}H-n.m.r. spectrum of S11(:), the presence of a surface active impurity was apparent from surface tension measurements. When the surface tension of an aqueous solution of S11(:) was measured as a function of the S11(:) concentration, an anomalous dip around the cmc was observed. This phenomenon is typical for the presence of a surface active contamination like C11(:)OH, even if its concentration is only 0.5% of the surfactant concentration[36]. After two recrystallization steps, the minimum in the surface tension curve was not present anymore indicating a sufficient purity of S11(:).

The cmc of S11(:), determined with conductivity and surface tension measurements, was 29.7 ± 1.2 and 28.2 ± 1.7 mM ($n = 3$, ± sd) respectively. These values are in good agreement with the theoretically expected value of 26 mM obtained from the Klevens equation, $^{10}\log(\text{cmc}) = A - Bn_c$ with n_c the number of carbons in the chain of a homologous series of a surfactant type. In this equation $A = 1.42$ and $B = 0.30$ for n-alkyl-1-sodium sulfates[37]. Mathematically, it must be taken into account that the introduction of a double bond in the chemical structure of a surfactant is almost equivalent to the removal of one CH$_2$ group from a fully saturated chain[38,39]. Therefore n_c was taken as 10.

Coating of S11(:) and SDS onto PE

PE samples were immersed in an aqueous solution of 0.20 M S11(:) or SDS containing 1 vol.% of hexanol and then dried. Hexanol was added to obtain complete wetting of the PE surfaces by the coating solution. Complete wetting is essential to obtain polymeric samples onto which the surfactant is deposited after removing the samples from the coating solution[40]. XPS analysis of these samples showed substantial amounts of oxygen (O 1s), sulfur (S 2p), and sodium (Na 1s) at their surface (*Table 1*). This shows that it is possible to coat both types of surfactant onto the PE surface. The binding energy of the S 2p electrons was 169.0 ± 0.1 eV. This corresponds well with the reported binding energy of 169.1 eV for the S 2p electrons of sulfate groups[30].

The atomic percentages of sodium and sulfur at the surface of PE/S11(:) and PE/SDS samples do not correspond with each other although the number of sodium and sulfur atoms in the surfactants are the same. This is caused by the fact that the XPS sampling depth is larger than the layer of coated surfactant. The thickness of a coated surfactant layer (d) could be calculated from the XPS data using an overlayer model. In this model it was assumed that the surfactants were randomly oriented on the PE surface[40]. A thickness of 40 ± 11 and 62 ± 14 Å was calculated for a coated layer of S11(:) and SDS on PE respectively.

When the PE/S11(:) and PE/SDS samples were washed with an aqueous solution of 0.1 mM HCl and analysed with XPS, only a small amount of oxygen was detected at their surface which was the same as the amount of oxygen at the surface of untreated PE (*Table 1*). Thus all of the coated material was removed upon washing.

Plasma treatment of PE, PE/S11(:), and PE/SDS samples

PE, PE/S11(:), and PE/SDS samples were treated with a static argon plasma and the surfaces were analysed with XPS. During the argon plasma treatment, different processes occur simultaneously, namely etching and oxidation. Due to vacuum ultraviolet (UV) irradiation and the collision of argon metastables and ions with a polymeric sample, etching of the surface takes place. This was reflected in a gradual decrease in the atomic percentage of sulfur at the PE/S11(:) surface upon plasma treatment (*Figure 1*). At the same time processes are taking place that induce oxidation of the surface. Free radicals are produced during the plasma treatment. These radicals can react with oxygen when the plasma treated surface is exposed to air. Direct surface oxidation is also possible if an oxygen source, like e.g.

adsorbed water or a small air leakage, is present during plasma treatment. The occurrence of these processes resulted in the introduction of oxygen at the polymeric surfaces as was observed for PE. Due to oxidation of the surface, the relative decrease in the atomic percentage of oxygen at plasma treated PE/S11(:) surfaces as a function of plasma treatment time is relatively smaller than the decrease in the atomic percentage of sulfur.

The plasma treated PE/S11(:) and PE/SDS samples were washed with an aqueous solution of 0.1 mM HCl to remove any material that was not immobilized on the surface. Besides oxygen, also sulfur was detected at the surface of plasma treated and washed PE/S11(:) and PE/SDS samples (*Figure 2*). This clearly indicates that immobilization occurred. The atomic percentage of sulfur on the plasma treated and washed PE/S11(:) samples initially increased with plasma treatment time, reached a maximum of 0.57 at.% at a plasma treatment time of 5 s, and subsequently decreased. The atomic percentage of sulfur at the plasma treated and washed PE/SDS surfaces showed the same trend but the maximum of 0.17 at.% sulfur was much lower.

The binding energy of the S 2p electrons was (168.9 ± 0.2) eV. This is similar to the binding energy of the S 2p electrons from precoated samples before plasma treatment. The binding energy of the S 2p electrons indicate that the sulfate groups were not chemically modified during argon plasma treatment. If the sulfate groups would have been transformed in for example sulfonate or sulfonic acid groups, a lower binding energy of the S 2p electrons (168.0–168.3 eV) would have been observed. Consequently, it can be concluded that both S11(:) and SDS could be immobilized on PE by means of an argon plasma treatment without affecting the sulfate groups.

Table 1 XPS analysis of PE samples, PE samples that were coated with S11(:) (PE/S11(:)) or SDS (PE/SDS), and PE/S11(:) and PE/SDS samples that were washed with an aqueous solution of 0.1 mM HCl ($n \geq 3$, ± sd)

Film	at.% O	at.% S	at.% Na
PE	0.2 ± 0.3	—[a]	—[a]
PE/S11(:)	19.0 ± 2.0	3.0 ± 0.6	5.2 ± 0.6
PE/S11(:),washed	0.3 ± 0.2	—[a]	—[a]
PE/SDS	18.2 ± 1.2	4.5 ± 0.3	5.4 ± 0.4
PE/SDS,washed	0.2 ± 0.3	—[a]	—[a]

[a] No peaks were observed in the detail scans of the S 2p (160–180 eV) or Na 1s (1060–1080 eV) regions
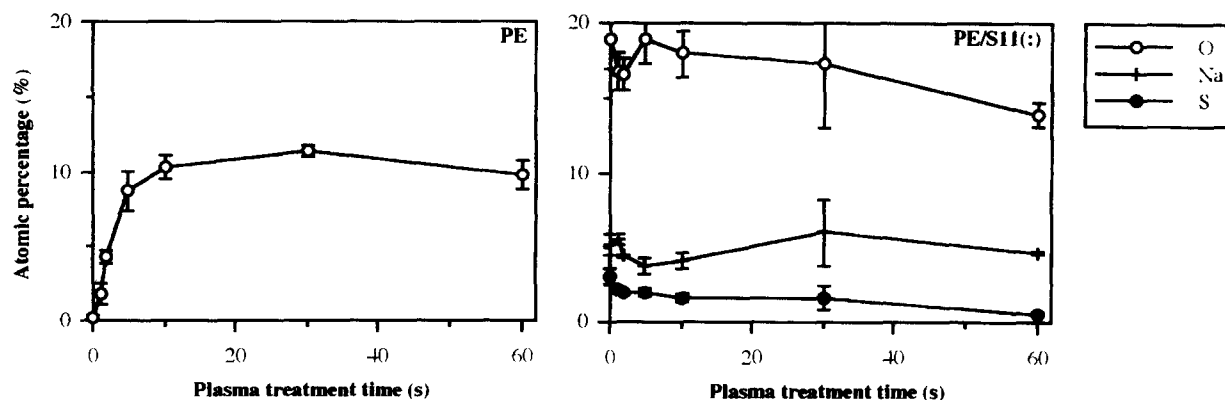

Figure 1 XPS analysis of PE and PE/S11(:) samples that were treated with an argon plasma. The samples were not washed after plasma treatment. The atomic percentages of oxygen, sodium, and sulfur are given as a function of the plasma treatment time ($n \geq 3$, ± sd)

No sodium was detected on the plasma treated and washed PE/S11(:) and PE/SDS samples. This was also reported for plasma treated and washed PP/SDS samples that contained sulfate groups at the surface. This phenomenon was attributed to the exchange of the sodium ions by protons during washing of the samples with a sodium deficient medium[26].

From the occurrence of a maximum in the atomic percentage of sulfur on the plasma treated and washed PE/S11(:) and PE/SDS samples as a function of the plasma treatment time the competition between etching and immobilization of the surfactant molecules on the surface is clear. Upon plasma treatment the surfactants are immobilized on the surface and the atomic percentage of sulfur increases. Due to simultaneous etching, sulfate groups are removed from the surface and this leads to the decrease in the atomic percentage of sulfur at the surfaces.

The results of the immobilization of S11(:) and SDS can be compared by calculating the immobilization efficiency of both surfactants on PE. The immobilization efficiency is defined as the percentage of the amount of sulfate groups, which are present in the initially coated surfactant layer, that is retained at the PE surface. Since the sulfate groups of the surfactants were not modified during the plasma treatment, the atomic percentage of sulfur on the PE/S11(:) and PE/SDS samples after coating (*Table 1*) and after plasma treatment and washing (*Figure 2*) can be used to calculate the immobilization efficiency. The immobilization efficiency of S11(:) on PE reached a maximum of 25.3 ± 5.0% at a plasma treatment time of 5 s compared to only 6.2 ± 0.6% for SDS (*Figure 3*). With these data, the density ($r =$ 0.99 g/cm^3 for both surfactants), the molecular weights of the surfactants, and the thickness of the initially coated surfactant layer, the maximum surface density of sulfate
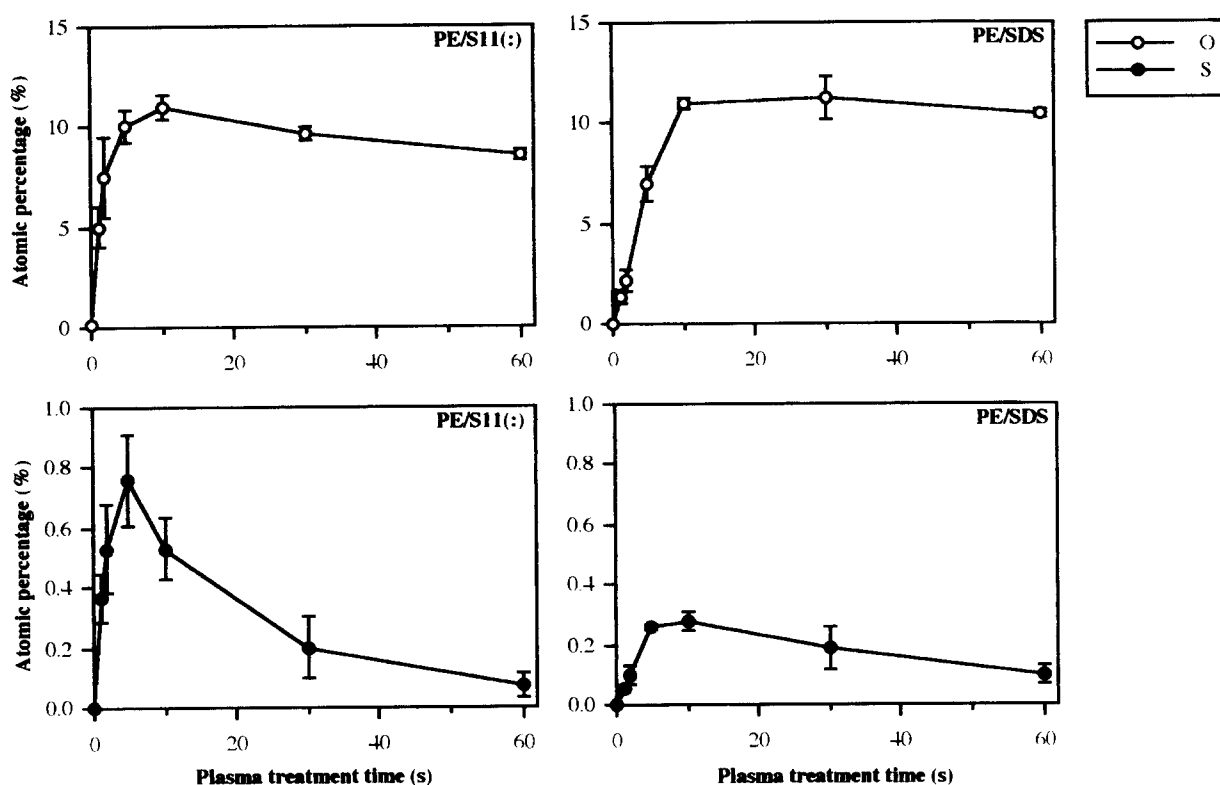

Figure 2 XPS analysis of PE/S11(:) and PE/SDS samples that were treated with an argon plasma and washed with an aqueous solution of 0.1 mM HCl. The atomic percentages of oxygen and sulfur are given as a function of the plasma treatment time ($n \geq 3$, ± sd)
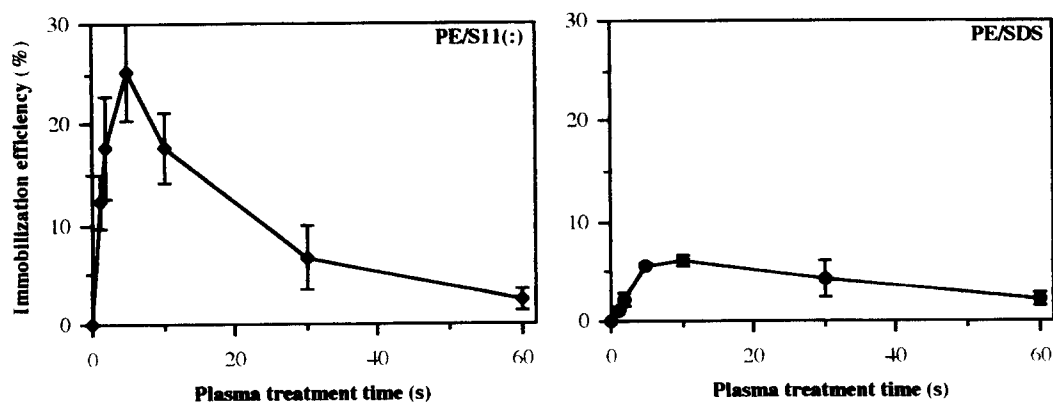

Figure 3 The immobilization efficiency of S11(:) and SDS on PE given as a function of the argon plasma treatment time ($n \geq 3$, ± sd)
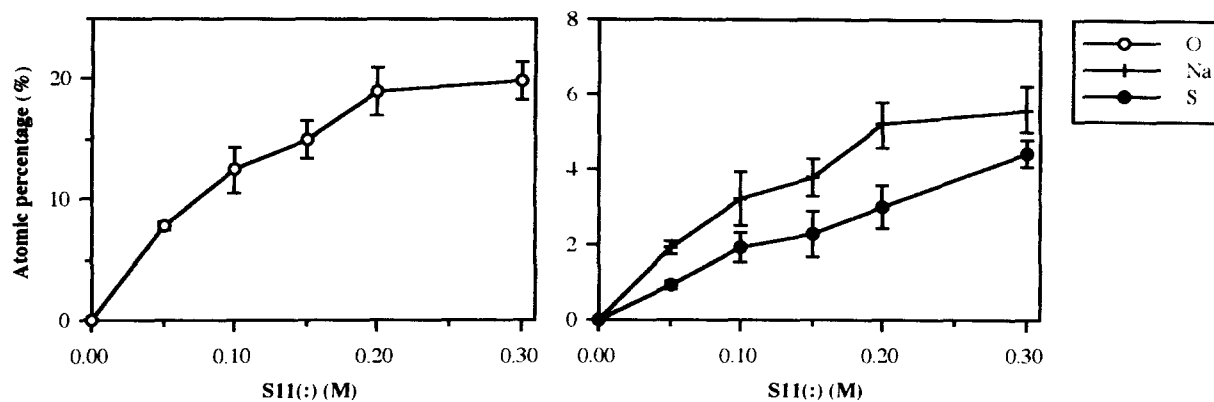
Figure 4 XPS analysis of PE/S11(:) samples. The atomic percentages of oxygen, sodium, and sulfur are given as a function of the S11(:) concentration in the coating solution ($n \geq 3$, ± sd)

groups at the surface of modified PE can be calculated[27]. This results in densities of one sulfate group per 45 and 127 Å^2 for plasma treated and washed PE/S11(:) and PE/SDS samples respectively.

By comparison of the immobilization efficiency of S11(:) and SDS, it can be concluded that the presence of a double bond in the alkyl chain enhances the efficiency of the immobilization. Similar results were obtained for the immobilization of the sodium salts of unsaturated and saturated fatty acids on PE with the use of an argon plasma treatment[27]. Maximum values of the immobilization efficiency of sodium 10-undecenoate (C11(:)) and sodium dodecanoate (C12) were also observed at a plasma treatment time of 5 s under identical plasma treatment conditions. The maximum immobilization efficiencies of C11(:) and C12 were 28 ± 6 and 6 ± 3% respectively. Therefore it is likely that immobilization of the carboxylate and sulfate group containing surfactants on PE proceeds by the same mechanisms. A possible mechanism involves the generation of radicals both at the PE surface and on the alkyl chains of the surfactants by the argon plasma[41,42]. When these radicals recombine, a covalent bond between the surface and the surfactant is formed. Additionally, the terminal double bond of unsaturated surfactants can be opened by surface radicals by which the unsaturated surfactants are covalently coupled to the polymeric substrate. Apparently, the latter mechanism predominantly proceeds in the case of immobilization of unsaturated surfactants.

The results of the immobilization of sulfate and carboxylate containing surfactants with aliphatic chains of the same chemical structure on one particular substrate are very similar. However, this is not the case for the immobilization of a surfactant on different substrates. In this study only 6% of the initial amount of coated SDS was immobilized on PE whereas an immobilization efficiency of about 25% for SDS on PP has been reported[26]. However, the experiments described in the latter study were performed under different plasma treatment conditions and with different equipment. This clearly points out that many factors are important in the immobilization of surfactants on polymeric surfaces with the use of an argon plasma treatment.

Influence of the thickness of the surfactant layer on its immobilization

The immobilization efficiency of S11(:) on PE as a function of the thickness of the initially coated surfactant layer was also investigated. For this purpose, PE samples were precoated from solutions with varying concentrations

of S11(:) (*Figure 4*). XPS analysis showed that upon increasing the S11(:) concentration in the coating solution the atomic percentages of oxygen, sulfur, and sodium on the resulting PE/S11(:) samples increased. These increases are indicative for an increase in the layer thickness of coated material (*Figure 5*)[40].

The precoated samples were subsequently treated with an argon plasma for 5 s, washed with an aqueous solution of 0.1 mM HCl, and analysed with XPS (*Figure 6*). As for the precoated samples, the atomic percentage of sulfur at the surface of plasma treated and washed PE/S11(:) samples increased gradually with increasing S11(:) concentration in the coating solution. A maximum in the atomic percentage of sulfur was obtained by plasma treating PE/S11(:) samples precoated from a solution of 0.20 M S11(:). A further increase in the S11(:) concentration of the coating solution decreased the final atomic percentage of sulfur at the surface after plasma treatment and washing. The atomic percentage of oxygen on the plasma treated and washed PE/S11(:) samples precoated from a solution of 0.30 M was significantly lower than on the other samples. The lower oxygen content can be explained by the fact that substantial amounts of the oxygen containing groups introduced during or after the plasma treatment are present on the precoated overlayer. Since a relatively large amount of this layer is not immobilized on this sample, more oxygen containing groups are washed off from the surface.

The values of the immobilization efficiency of S11(:) on PE for layer thicknesses below 40 Å were not significantly different from each other (*Figure 7*). The immobilization efficiency for PE/S11(:) samples with an initial layer thickness of 63 Å was significantly lower ($p < 0.05$) than
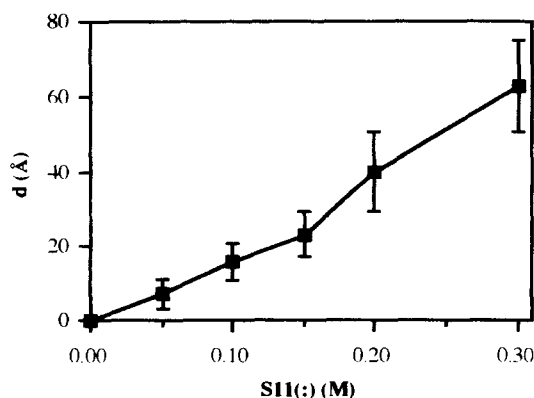

Figure 5 Thickness of a coated S11(:) layer on PE as a function of the S11(:) concentration in the coating solution ($n \geq 3$, ± sd)
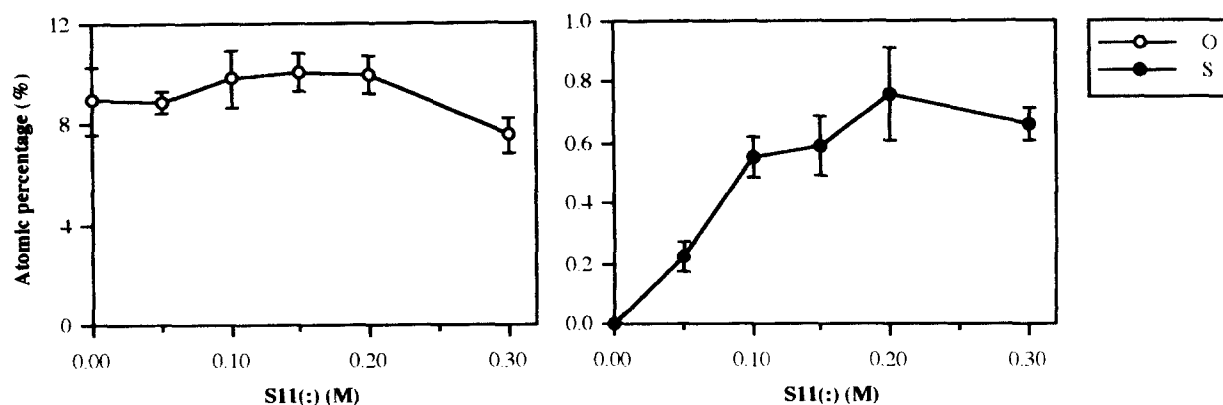
Figure 6 XPS analysis of PE/S11(:) samples that were treated with an argon plasma for 5 s and washed with an aqueous solution of 0.1 mM HCl. The atomic percentages of oxygen and sulfur are given as a function of the S11(:) concentration in the coating solution ($n \geq 3$, $\pm$ sd)
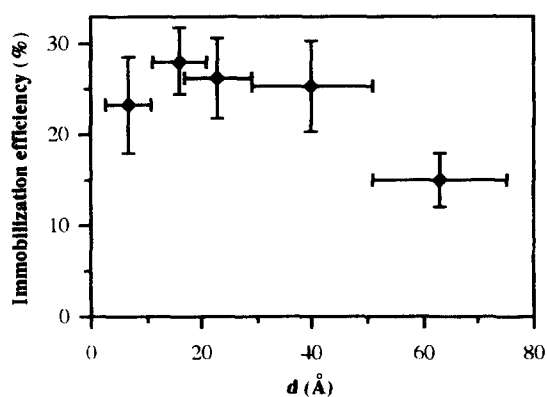

Figure 7 The immobilization efficiency of S11(:) on PE given as a function of the thickness of the S11(:) layer initially coated onto the PE surface ($n \geq 3$, $\pm$ sd)

for the other samples. This might indicate that the immobilization efficiency is dependent on the thickness of the initially coated surfactant layer.

As suggested above, radicals seem to play a predominant role in the immobilization process. Less radicals might be formed on the polymeric substrate during plasma treatment when a thicker layer of coated material is present on the surface. However, UV-radiation emitted by the plasma, which plays a predominant role in the formation of radicals at the surface, has a penetration depth of 1–10 mm[43,44]. Therefore it is more likely that upon increasing the layer thickness of coated material, part of the surfactant molecules are located too far away from the surface and

cannot be immobilized through a reaction with surface radicals.

Consequently, the low immobilization efficiencies of SDS on PE (see previous section) may also partly be the result of a relatively thick SDS layer compared to the S11(:) layer on PE. However, this effect will only be of minor importance compared to the effect of the differences in the chemical structure of the aliphatic chain of the surfactants[41].

Contact angle determinations

The wettability of different modified polymeric samples was investigated by determining the dynamic water contact angles (*Figure 8*). Plasma treated and washed PE samples (PE-Ar 5) contained oxygen due to oxidation during and/or after the plasma treatment (*Figure 1*). Consequently, their surfaces were more hydrophilic than the original PE samples. Plasma treated and washed PE/SDS samples contained a comparable atomic percentage of oxygen relative to the PE-Ar 5 samples and only a small amount of sulfate groups. Therefore the advancing and receding contact angles of both samples were comparable. No significant differences were observed between the advancing contact angles of PE-Ar 5 and plasma treated and washed PE/S11(:) samples. However, the receding contact angles of the latter were significantly lower. Since the atomic percentage of oxygen on all of the plasma treated and washed samples was comparable, this effect is attributed to the presence of a substantial amount of sulfate groups at the surface.

The difference between the advancing and receding contact angles is known as the contact angle hysteresis. The
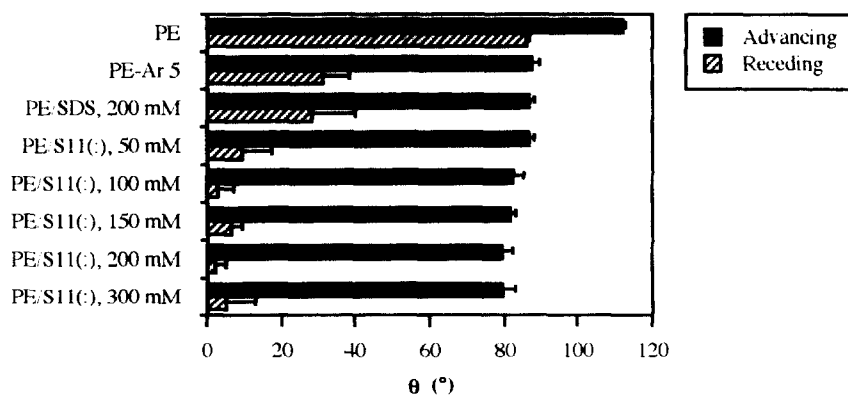

Figure 8 The advancing and receding water contact angles of PE and several polymeric samples (PE, PE/SDS, and PE/S11(:) precoated from solutions of varying concentrations) that were treated with an argon plasma for 5 s and subsequently washed with an aqueous solution of 0.1 mM HCl ($n = 3$, $\pm$ sd)

large hysteresis of the plasma treated and washed samples is caused by a combination of the presence of polar groups at the surface and their reorientation under influence of the liquid phase[45–48]. The polar groups are initially turned away from the solid/air interface but, when immersed in an aqueous solution, they reappear at the interface. Therefore the presence of sulfate groups influences the receding contact angle, whereas this influence is not observed in the advancing contact angles.

CONCLUSIONS

Sodium 10-undecene sulfate (S11(:)) was successfully synthesized by sulfating 10-undecene-ol with the use of the pyridine-SO_3 complex. Elemental analysis, sulfate group titration, ^{1}H-n.m.r., *FT*i.r. spectroscopy, and surface tension measurements showed that the synthesized product was of high purity. S11(:) and sodium dodecyl sulfate (SDS) could be immobilized on poly(ethylene) (PE) by means of an argon plasma treatment. No other sulfur containing functional groups than sulfate groups were introduced at the surface. At an optimal plasma treatment time of 5 s, about 25% and 6% of the initial amount of sulfate groups in the coated S11(:) layer and SDS layer respectively was retained at the polymeric surface. This is in close agreement with a previous study, where similar results were obtained with saturated and unsaturated carboxylate group containing surfactants. Increasing the thickness of the initial coated surfactant layer resulted in a decrease in the immobilization efficiency at layer thicknesses of more than 40 Å.

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