

Removal of Pendant Groups of Vinyl Polymers by Argon Plasma Treatment

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Poly(acrylic acid) (PAAc) and poly(vinyl chloride) (PVC) were treated with an argon plasma to create unsaturated bonds at the surface. By use of X-ray photoelectron spectroscopy and Fourier transform infrared measurements, it was shown that the pendant groups of these polymers are removed by the argon plasma treatment. This resulted in the formation of unsaturated bonds and cross-links in the modified layer. It was found that the removal of the pendant groups is induced by UV light emitted by the argon plasma. During treatment of PAAc decarboxylation took place, which made the argon plasma more oxidative in character. The modified layer was reoxidized and eventually the PAAc surface was ablated with time. The removal of chlorine from PVC was found to be preferential, and a highly cross-linked layer, containing at least 15% unsaturated bonds, was obtained. The outermost top layer of this modified layer became oxidized after exposure to air due to a reaction between long-living radicals and oxygen.

Introduction

Glow discharge processes (e.g., corona and low-pressure plasma treatments) are frequently used to modify the surface properties of engineering plastics.^{1–8} These processes have certain advantages over other surface-modifying techniques such as flame treatment, ultraviolet (UV)^{9–12} and γ -irradiation,¹³ and wet chemical treatments.^{14–16} For instance, the modification depth is small, and complex geometries can be treated in one step without the use of solvents.^{3,7,17–23} Furthermore, a broad range of surface properties can be obtained, although the specificity toward the type of functional groups introduced at the

surface is considered to be low.^{1,24,25} Some improvements have been made by preadsorbing surfactants on polymeric substrates followed by a gas plasma treatment.^{23,26,27}

In earlier studies, it was shown by optical emission spectroscopy (OES) measurements that, upon argon plasma treatment of PAAc, decarboxylation took place.^{28,29} This resulted in the presence of CO, CO₂, and water in the plasma phase. It was found that decarboxylation was induced by the vacuum UV (wavelength < 150 nm) emitted by the argon plasma. In principle, the preferential removal of pendant groups from vinyl polymers may lead to the formation of unsaturated bonds. After the plasma treatment, these could be used for example in grafting or the transport of electricity. In the case of PAAc, removal of the polymer layer was also observed (i.e., etching). From the literature, it is known that oxidation processes can result in etching of the treated polymer.^{9,24} The observed ablation of PAAc may therefore be due to the oxidative environment caused by the release of oxygen-containing species in the plasma phase. This oxidation can be minimized by a pulsed plasma treatment based on the

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assumption that the oxygen-containing species are removed from the reactor by the argon flow during the "off" time between two pulses.

The pendant group in a vinyl polymer [e.g., poly(vinyl alcohol) (PVA), -chloride (PVC), -fluoride (PVF), Polystyrene (PS)] can also be selected to obtain a highly unsaturated surface and to minimize reoxidation or ablation or both. Considering the results found for PAAc, oxygen-containing pendant groups as in PVA are not interesting alternatives. A disadvantage of PS is the stability of the pendant phenyl group, which makes selective removal of this group difficult. To obtain selective removal of the pendant group, volatile compounds should be formed. From PVF and PVC, volatile compounds such as HF and HCl can easily be formed. Of these two polymers, PVC seems to be the most promising substrate as the carbon-chlorine bond has a lower energy compared with the carbon-fluorine bond.

In the literature, several studies on the effect of γ -radiation,^{13,30–34} UV irradiation,^{35,36} ion beam^{37,38} and electron beam³⁹ treatment on the surface properties of PVC have been published. It was found that the carbon-chlorine bond in PVC is readily cleaved. Furthermore, unsaturated structures were observed after treatment. Most of the species used for treatment in the cited studies are also present in an argon plasma (e.g., electrons, ions, and UV). Although the energy of these species in a plasma may be quite different, a similar effect of an argon plasma treatment on PVC might be expected.⁴⁰ Furthermore, the plasma technique is relatively simple, only modifies the surface, and offers the possibility to treat large surface areas in one step.

The aim of the present study was to introduce unsaturated bonds at the surface of vinyl polymers by an argon plasma treatment. To investigate this, argon plasma treated PAAc and PVC samples were characterized with X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy. Furthermore, the argon plasma treated samples were extracted with the appropriate solvents, and the residual insoluble layer was analyzed with FTIR and solid-state NMR (SSNMR).

Experimental Section

Materials. PAAc (M_w 250 000) and PVC (M_w 97 000, M_n 55 000) were purchased from Aldrich Chemie (Brussels, Belgium). All solvents were of analytical grade purity and were purchased from Merck (Darmstadt, Germany). Bromine was of synthetic grade purity (99%) and was obtained from Merck (Darmstadt, Germany). Argon (purity $\geq 99.999\%$) was obtained from Hoekloos (Schiedam, The Netherlands). Water used was doubly deionized. All chemicals were used as received. Glass disks (diameter 2.5 cm) with a sputtered chromium and gold layer were supplied by the Department of Applied Physics and Electrical Engineering (University of Twente, Enschede, The Netherlands). Glass disks

(diameter 1.5 cm) were purchased from Knittel Waldemar (Braunschweig, Germany).

Cleaning. All glassware, substrates, and tools were cleaned ultrasonically consecutively three times in toluene, acetone, water, and acetone and subsequently dried in vacuo at room temperature.

Spin Coating. PAAc and PVC were dissolved in methanol and THF, respectively, to a concentration of 2% w/w. Spin coating was carried out at 2000 rpm using a Teflon sample holder mounted on an IKA RW 20 DZM mechanical stirrer (Janke & Kunkel, Staufen, Germany). A volume of 0.025 mL of the polymer-containing solution was dropped on rotating glass disks with a diameter of 1.5 cm. For disks with a diameter of 2.5 cm, a volume of 0.05 mL was used. After rotating for 1 min, the spin-coated glass disks were taken out of the sample holder and dried overnight in vacuo at room temperature.

Casting. PAAc films were made by casting 250 mL of a 2% w/v solution of PAAc in methanol in a Petri-dish (diameter 19 cm). PVC films were made by casting a 30% w/w solution in THF on a glass plate with a casting knife (0.075 mm). After evaporation of the solvent at room temperature, the films were dried in vacuo at room temperature under a metal plate to keep the samples flat. Finally, the films were rinsed three times with hexane and dried in vacuo at room temperature.

Thickness Measurement. The thickness of spin-coated layers was determined with a Dektak IIA (Sloan Technology Corporation, Santa Barbara, CA). After removing the spin-coated layer from part of the substrate, the needle was moved over the boundary between the bare and the covered substrate. The height difference was taken as the thickness of the spin-coated layer. For the determination of the thickness of the cast films, an ID-C112B thickness meter (Mitutoyo, Japan) was used.

Plasma Treatment. The plasma apparatus has been described in detail in the literature.^{28,29} In short, it consists of a tubular reactor (internal diameter 6.5 cm, length 80 cm) with three externally placed, capacitively coupled electrodes. The two grounded (cold) electrodes were placed at a distance of 10 cm on either side of the powered (hot) electrode, which was placed in the center of the reactor. Typically, the procedure for an argon plasma treatment was as follows. The samples were placed on two glass plates, which were placed in the center between the hot and the cold electrodes. After pumping the reactor to a pressure $< 3 \times 10^{-6}$ mbar, it was flushed with an argon flow (10 sccm/min, 0.08 mbar) for 15 min. The samples were then treated with either a continuous or a pulsed (0.1 s on, 8.5 s off) plasma (13.56 MHz, 50 W, 10 sccm/min, 0.08 mbar) for a predetermined time. After the plasma treatment, the argon flow was maintained for 2 min, after which the reactor was brought to atmospheric pressure with air. All treated samples were stored at -18°C .

Extraction of Plasma Treated Films. The insoluble fractions of argon plasma treated films (300 s) of PAAc and PVC were obtained by extracting the films (about 10 PAAc films, 2.5 cm \times 2.5 cm; 10–15 PVC films, 4 cm \times 10 cm) at room temperature in 5 mL/film of methanol (PAAc) or THF (PVC). After gentle stirring and sedimentation of the insoluble fraction, the solvent was removed with a pipet and refreshed. This was done five times, after which the insoluble fraction was filtered off (glass filter no. 5). After thorough washing with solvent (± 500 mL) the insoluble fraction was dried in vacuo at 35°C .

The thickness of the insoluble layer can be calculated by

$$d = M/(A\rho) \quad (1)$$

where M is the mass of the insoluble fraction [kg], A is the total surface area of the films used for extraction [m^2], ρ refers to the density of the polymer [kg/m^3],⁴¹ and d is the thickness of the insoluble layer [m]. In eq 1, it is assumed that the insoluble layer has the same density throughout, equal to that of the pristine polymer, and that this layer is totally insoluble.

Reaction of Unsaturated Bonds with Bromine. Unsaturated bonds at the surface were reacted with Br_2 vapor. A polymeric sample was placed on glass beads in a glass vial. Subsequently, a drop of Br_2 was injected under the sample between the glass

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Table 1. Thicknesses of Spin Coated Layers and Cast Films of PAAc and PVC and Chemical Composition^a of PAAc and PVC sample

substrate	PAAc	PVC
disk diam 1.5 cm	0.17 ± 0.03 μm	0.24 ± 0.01 μm
disk diam 2.5 cm	0.23 ± 0.02 μm	0.28 ± 0.01 μm
casting	374 ± 93 μm	61 ± 7 μm
% C	60.4 ± 0.6	69.8 ± 0.8
% O	39.6 ± 0.6	1.1 ± 0.5
% Cl	—	29.1 ± 1.1

^a Determined with XPS; no other signals were detected.

beads. The vial was closed, and the reaction was allowed to proceed in the dark for 1 min at room temperature. After evaporation of adsorbed Br₂, the sample was stored at -18 °C and subsequently analyzed with XPS. Because an extra element is taken into account in the calculation of the atom concentrations, the concentrations of the other elements should decrease proportionally.

Characterization. XPS measurements were carried out on either spin-coated glass disks (diameter 1.5 cm) or cast films using a Kratos XSAM 800 (Manchester, UK) equipped with a Mg K α source (1253.6 eV). The analyzer was placed perpendicular to the sample surface. The input power was 150 W (10 mA, 15 kV). The analyzed spot size was 3 mm × 6 mm. Survey scans [1100–0 eV binding energy (BE) window] were recorded with a pass energy (PE) of 100 eV and a dwell of 0.1 s. Relative peak areas for the different elements were calculated by numerical integration of the detail scans (20 eV BE window, 50 eV PE) using sensitivity factors given in the literature.⁴² After normalization, the concentrations of the various elements were obtained.

FTIR spectra were recorded from spin-coated glass disks (diameter 2.5 cm) using a BioRad FTS-60 (Cambridge, UK) in the reflectance mode. Background spectra were recorded using a clean substrate.

¹³C cross-polarization (CP)-mass SSNMR studies were performed on a Bruker MSL-400 NMR spectrometer (Bruker Canada Ltd., Milton, Canada), working at a 100.627 MHz ¹³C frequency, equipped with a 4 mm cross-polarization magic angle spinning (CP-MAS) probe. The spinning speed was 10 kHz. Cross-polarization experiments were performed under Hartman–Hahn conditions with a contact time of 2 ms and a recycle delay of 2 s. The $\pi/2$ proton pulse was 4.7 μs.

Results & Discussion

The results of the spin coating and casting of PAAc and PVC are summarized in Table 1 together with the results of the XPS measurements on untreated samples. The thickness of spin-coated layers on substrates used for XPS measurements (glass disks, diameter 1.5 cm) was around 0.20 μm. This means that no signals of the underlying substrate will be detected by XPS (measuring depth XPS is ±10 nm). Considering the error in the XPS measurement, the oxygen content of PAAc and the chlorine content of PVC are equal to the theoretical value (40.0 and 33.3%, respectively). Furthermore, PVC is slightly oxidized at the surface. Together with the absence of other signals in the XPS spectra, this shows that the samples do not contain any impurities.

The thickness of the spin-coated layers on substrates used for FTIR measurements [glass disks (diameter 2.5 cm) with a sputtered gold layer] was around 0.25 μm which is below the measuring depth of the technique (±1 μm).

The PAAc and PVC samples were treated with an argon plasma for different times. To study the effect of the argon plasma treatment time on PAAc and PVC, the chemical composition of the surface of untreated and argon plasma treated samples was determined with XPS (Figure 1). For PAAc, a decrease in oxygen content with increasing

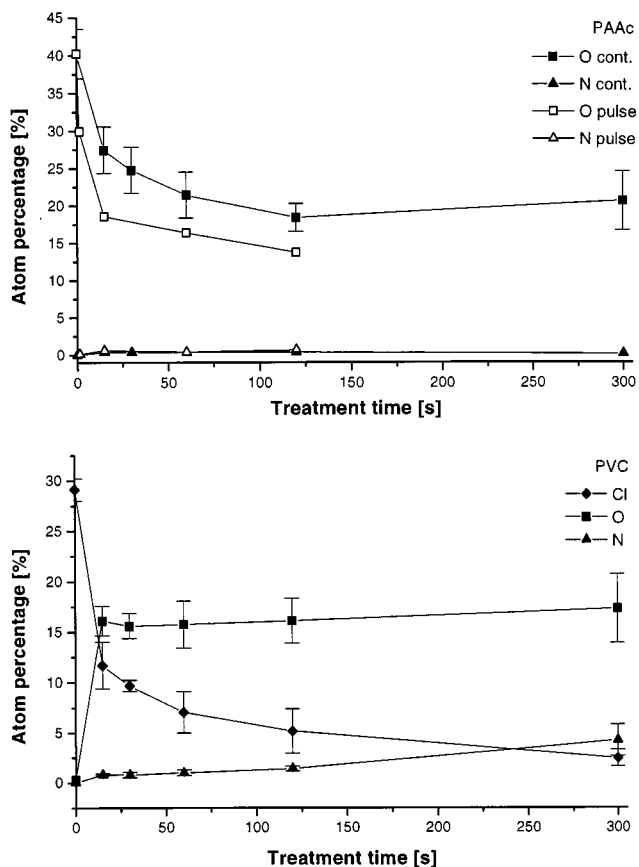


Figure 1. Top: Oxygen and nitrogen concentration (determined with XPS) at the surface of continuously ($n = 3 \pm \text{sd}$) and pulsed ($t_{\text{on}} 0.1 \text{ s}$; $t_{\text{off}} 8.5 \text{ s}$; $n = 1$) argon plasma treated PAAc samples as a function of treatment time. Bottom: Concentration of chloride, oxygen, and nitrogen (determined with XPS) at the surface of continuously argon plasma treated PVC samples as a function of treatment time ($n = 3 \pm \text{sd}$). Treatment time refers to the total plasma “on” time.

treatment time is found. At longer treatment times, the oxygen content seems to level off to around 20% for continuously plasma treated samples. These values are in good agreement with those found earlier.²⁹ For pulsed plasma treated samples, a decrease to around 15% is found. For both treatments, no nitrogen was incorporated.

The C 1s spectra (Figure 2) give additional insight into the chemical structure of the surface of the treated samples.⁴² Taking charging effects into account, the peaks at 287.1 and 291.2 eV in the C 1s spectrum of untreated PAAc can be assigned to carbon atoms in the polymer backbone and to carbon atoms in carboxylic acid groups, respectively.⁴³ The C 1s spectra of the argon plasma treated samples clearly show that the decrease in oxygen content is due to the removal of pendant carboxylic acid groups. Furthermore, for continuous plasma treated PAAc samples, the main peak shows a small broadening on the high BE side at longer treatment times, indicating the formation of other oxygen-containing groups.⁴³ This re-oxidation may be caused by oxygen-containing species which are released from the PAAc surface by the argon plasma treatment. Terlingen et al. already showed that CO, CO₂, and H₂O are present in the plasma phase when PAAc is treated with an argon plasma.^{28,29} Due to the presence of these oxygen-containing species, the argon plasma becomes more oxidative in character, probably

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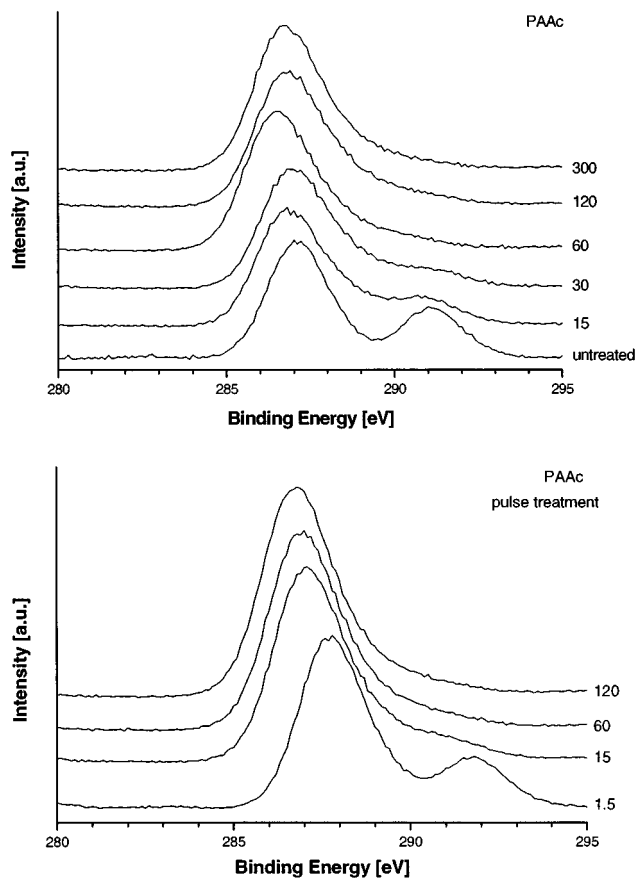


Figure 2. XPS C 1s spectra of untreated and continuously argon plasma treated PAAc (top) and pulsed (t_{on} 0.1 s; t_{off} 8.5 s) argon plasma treated PAAc (bottom) samples. The numbers refer to the total plasma "on" time (s).

resulting in the observed reoxidation of the surface. This suggestion is substantiated by the lower oxygen content found for the pulsed plasma treated samples (Figure 1). When a pulsed plasma is applied, the carboxylic acid peak disappears faster (cf. C 1s spectra of 15 s pulsed and continuous argon plasma treated samples). The oxygen-containing species in the plasma phase are removed between two pulses. Therefore, the argon plasma is not much altered, resulting in less reoxidation. An additional cause for the reoxidation might be the possible presence of adsorbed water on the reactor walls or on the PAAc films.

The chlorine content of the surface of argon plasma treated PVC decreases with increasing treatment time to about 3% after 300 s (Figure 1). In Figure 3, the charge-corrected C 1s spectra are depicted. Interestingly, the pristine polymer showed a charge shift, which was 1.2 eV higher than the plasma treated samples. This indicates that the surface conductivity of the plasma treated samples is higher, which might be due to the introduction of unsaturated carbon bonds. The C 1s peak of PVC is built up from signals of carbon atoms only attached to carbon and carbon atoms directly attached to chlorine.⁴³ Due to the low resolution, only one C 1s peak is visible in Figure 3 (top). The C 1s spectra show that the main peak is shifted to lower BE by the argon plasma treatment, probably due to the removal of chlorine. The removal of chlorine affects the position of the C 1s peak in two ways. First, due to the presence of chlorine, the carbon atoms only attached to carbon in PVC already show a shift of 0.7 eV compared to carbon atoms in, for example, polyethylene.⁴³ This gives rise to a shift when chlorine is removed. Furthermore,

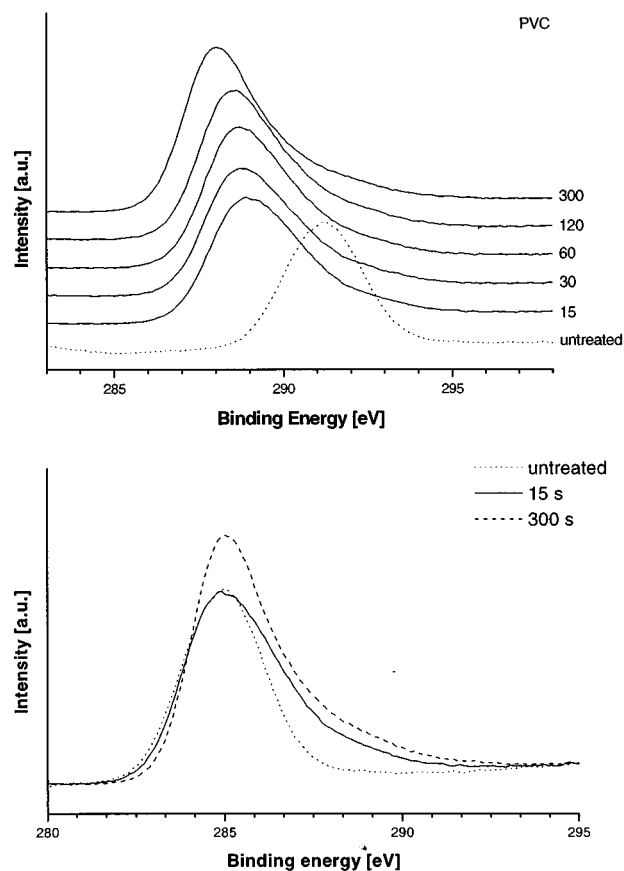


Figure 3. Top: XPS C 1s spectra of untreated (dotted line) and continuously argon plasma treated PVC samples. Charging effects were corrected by setting the Cl_{2p} peak at 202 eV. The numbers refer to the treatment time (s). Bottom: XPS C 1s spectra of untreated (dotted line), 15 s argon plasma treated (solid line) and 300 s argon plasma treated (dashed line) PVC samples. The maximum of the C 1s peaks was set at 285 eV.

when chlorine is removed from the surface, the contribution to the (combined) C 1s peak of carbon atoms attached to chlorine atoms will diminish and the maximum of the C 1s peak will shift to lower BE. Broadening of the C 1s peak upon longer plasma treatment times is illustrated by setting the maximum of the C 1s peaks to 285 eV (Figure 3, bottom).

On the argon plasma treated PVC samples, an oxygen content of 15–17% is found, almost independent of treatment time. The nitrogen content increases with treatment time (0–4%). Several processes may result in the observed oxygen and nitrogen contents. Most probably, oxygen and nitrogen are incorporated by a posttreatment reaction between air and long-living radicals in the PVC films.^{9,10} Other possibilities are that the incorporation of oxygen and nitrogen results from an air leak in the system or that the oxygen incorporation results from adsorbed water being desorbed during the argon plasma treatment. However, the C 1s peak (Figure 3, bottom) is only slightly broadened by the argon plasma treatment, indicating the formation of C–OH groups which are expected from a posttreatment reaction between radicals and air.⁴³ Higher degrees of oxidation (e.g., carbonyl and carboxylic acid groups) and a corresponding broader C 1s peak would be expected when water or air was present during the argon plasma treatment. Thus, the posttreatment oxidation reaction seems to be the major cause for the observed oxygen and nitrogen incorporation.

Both untreated and argon plasma treated PAAc and PVC films were derivatized with Br_2 to detect unsaturated

Table 2. Chemical Composition after Derivatization with Br₂^a of Untreated and Continuously Argon Plasma Treated PAAc and PVC Films (*n* = 1)

sample	O (%)	Cl (%)	Br (%)
PAAc, untreated	37.6		0.2
PVC, untreated	0.6	27.8	0.8
PAAc, 5 min Ar	17.1		5.9
PVC, 5 min Ar	18.7	1.5	7.3

^a Determined with XPS.

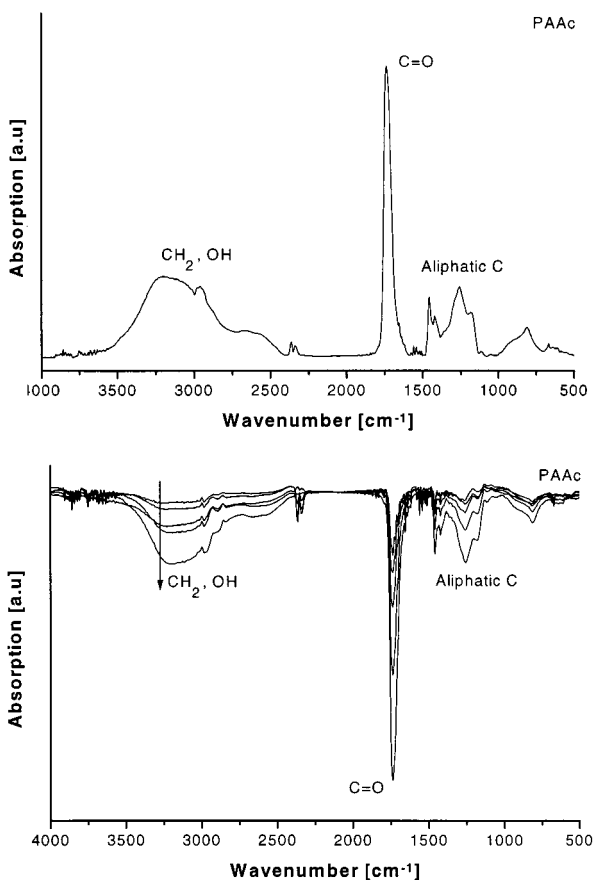


Figure 4. Top: FTIR spectrum of untreated PAAc. Bottom: Difference FTIR spectra of argon plasma treated PAAc samples. The difference spectra are calculated by subtracting the spectrum of the nontreated sample from that of the treated sample. The arrow indicates the direction of increasing treatment time (15, 30, 60, 120, and 300 s).

bonds. The results are summarized in Table 2. For both polymers, a significant increase in bromine content is observed after argon plasma treatment. From the amount of incorporated bromine, it can be calculated that for argon plasma treated PAAc about 7.7% of the carbon atoms is present in unsaturated C=C bonds, assuming that no side reactions have taken place. For argon plasma treated PVC, this amount is about 10%. The slightly lower oxygen and chlorine contents after plasma treatment and derivatization compared to those found without derivatization (see Figure 1) can be explained by the fact that an extra element is taken into account in the calculations of the atomic concentrations.

The measuring depth of the XPS technique is about 100 Å. Therefore, only information about the chemical composition of the uppermost surface is obtained. Reflectance FTIR was used to investigate the chemical structure of the whole layer. A FTIR spectrum of the samples was taken before and after argon plasma treatment. The spectrum of the nontreated sample was subtracted from

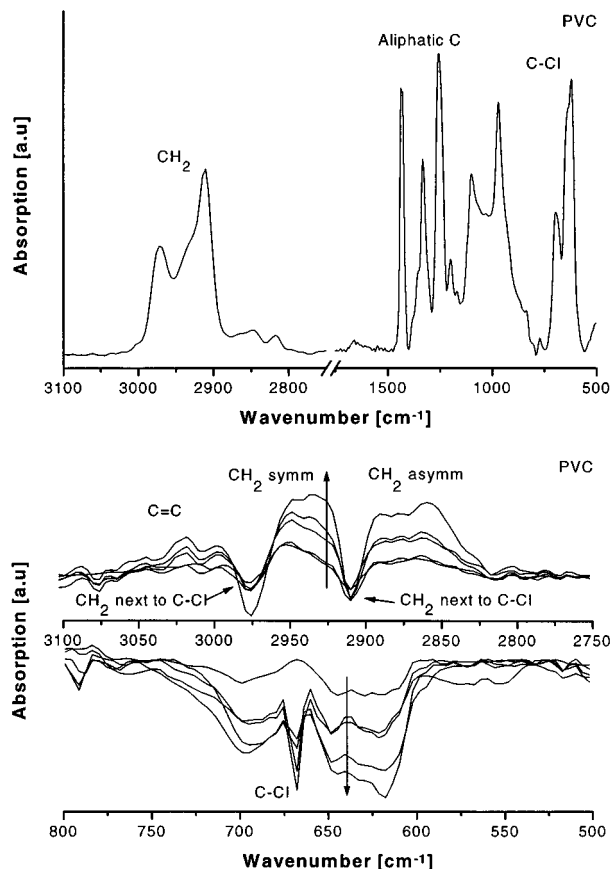


Figure 5. Top: FTIR spectrum of untreated PVC. Bottom: Details in the C–H and C–Cl absorption region of difference FTIR spectra of argon plasma treated PVC samples. The difference spectra are calculated by subtracting the spectrum of the nontreated sample from that of the treated sample. The arrows indicate the direction of increasing treatment time (15, 30, 60, 120, and 300 s).

the spectrum of the plasma treated sample. In this way, the net effect of the argon plasma treatment is made visible. These “difference” FTIR spectra of argon plasma treated PAAc are depicted in Figure 4 together with the spectrum of the untreated polymer. The absorption bands visible in the FTIR spectrum of untreated PAAc (Figure 4, top) can be assigned to aliphatic CH₂ groups (2930, 2850, 1450, and 780 cm⁻¹) and COOH groups (3200–3000, 1740, and 1250 cm⁻¹). In the difference spectra of argon plasma treated PAAc (Figure 4, bottom) these absorption bands are also visible as negative absorption bands. The intensity of all absorption bands in the difference spectra increases with increasing treatment time. Furthermore, no new absorption bands develop upon argon plasma treatment. Since the thickness of the spin-coated PAAc layer is below the measuring depth, this means that the PAAc layer is removed (i.e., etched) by the argon plasma treatment. The etching of PAAc was shown to be caused by the UV light generated by the argon plasma.^{28,29} Oxidative chain scission processes, induced by the liberated oxygen-containing species in the plasma phase, may also cause etching.^{24,25}

The absorption bands in the FTIR spectrum of untreated PVC (Figure 5, top) can be assigned to aliphatic CH₂ groups (2975, 2910, 1430, and 970 cm⁻¹) and C–Cl groups (695 and 617 cm⁻¹). For the argon plasma treated PVC samples, some details of the difference FTIR spectra are pointed out (Figure 5, bottom). With increasing treatment time, the absorption bands at 695, 667, and 617 cm⁻¹ and at 2975 and 2910 cm⁻¹ decrease in intensity. These cor-

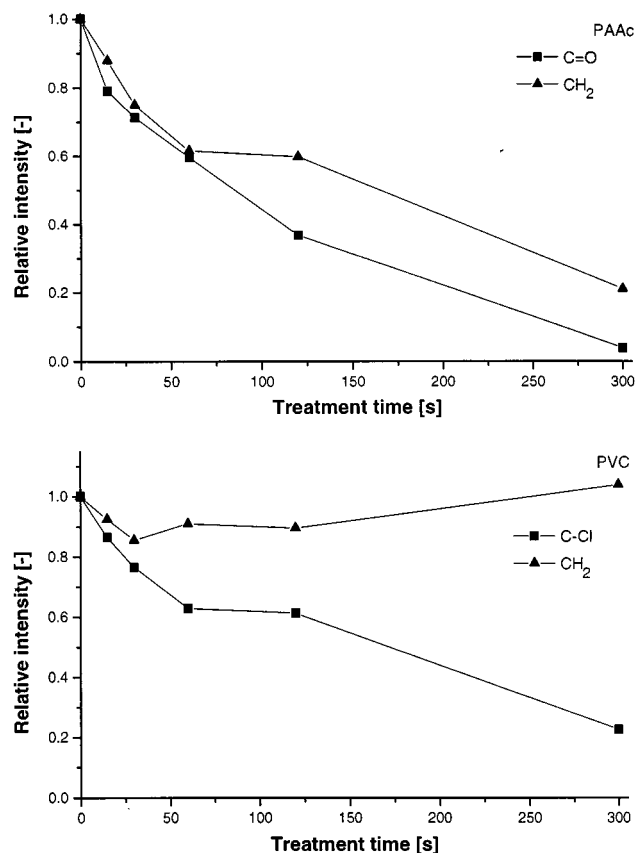


Figure 6. FTIR absorption band intensities of carbonyl (C=O, 1740 cm^{-1}), methylene (CH_2 , 2910 cm^{-1}) and chloride (C-Cl, 617 cm^{-1}) groups of argon plasma treated PAAc (top) and PVC (bottom) samples, relative to the intensities of the corresponding absorption bands of the untreated samples, as a function of treatment time.

respond with C-Cl groups and CH_2 groups next to C-Cl groups, respectively. Furthermore, some new absorption bands develop at 3020 cm^{-1} and at 2930, 2890, and 2860 cm^{-1} . These can be assigned to C=C-H and aliphatic CH_2 groups, respectively. From the FTIR spectra, it can be calculated that after 300 s about 80% of the chlorine is removed. In combination with the XPS results (90% removed after 300 s; see Figure 1), it can be concluded that chlorine is removed evenly throughout a layer of at least 0.25 μm . At this depth, only the UV light emitted by the argon plasma can be responsible for the removal of chlorine. Other plasma species (e.g., ions and electrons) do not have sufficient energy to penetrate that far into the polymer.

In Figure 6, the intensities of absorption bands corresponding with some characteristic groups of PAAc (CH_2 and C=O) and PVC (CH_2 and C-Cl) after argon plasma treatment are plotted relative to the intensities of the same absorption bands before argon plasma treatment. Figure 6 clearly shows the etching of the PAAc layer. Both the backbone CH_2 and the pendant carboxylic acid groups are removed by the argon plasma treatment.

In the case of PVC, the removal of chlorine is more preferential. Only the chlorine is removed while the concentration of the backbone CH_2 groups is almost constant.

From the literature, it is known that upon (argon) plasma treatment of polymers cross-linking may occur.^{3,24,44} The cross-linked layer is not soluble in the solvent for the unmodified polymer. To get an indication of the thickness of the modified layer the argon plasma treated

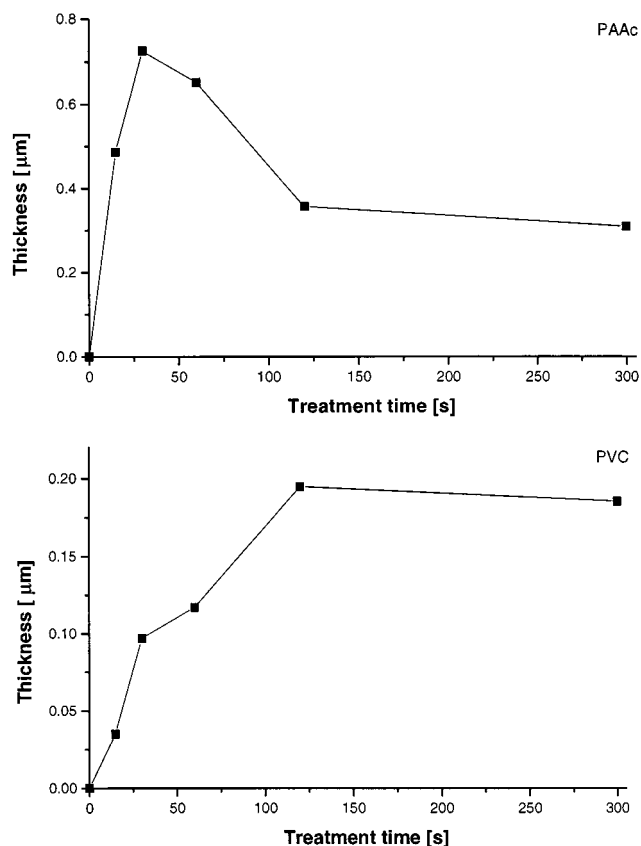


Figure 7. Thicknesses (calculated by eq 1) of the insoluble layers (obtained by extraction) of continuously argon plasma treated PAAc (top) and PVC (bottom) films as a function of treatment time ($n = 1$).

PAAc and PVC films were extracted with methanol and THF, respectively. The thicknesses of the insoluble layers were calculated from the obtained masses of the residual insoluble fractions and are depicted in Figure 7 as a function of treatment time. For PAAc, the thickness of the insoluble layer reaches a maximum after which it decreases again. For longer treatment times, it seems to level off to 0.3 μm . The insolubility of the layer is most probably caused by cross-linking, although the formation of unsaturated bonds, as observed with derivatization XPS, may also lower the solubility. The course of the thickness of the insoluble layer with plasma treatment time indicates that in the early stages of the plasma treatment mainly modification is taking place. The results of the pulsed treatments (Figure 1) suggest that the pendant carboxylic acid groups are removed in the early stages of the treatment. This results in the formation of unsaturated bonds and cross-links. However, upon prolonged continuous treatment, the released oxygen-containing species cause ablation of this modified layer. Eventually, an equilibrium between modification and ablation (i.e., a surface renewal) seems to be reached.

The thickness of the insoluble layer of argon plasma treated PVC initially increases with treatment time and levels off to 0.19 μm at longer treatment times. This again shows that UV light emitted by the argon plasma is the main cause for the modification.

Information about the chemical structure of the insoluble fractions of the argon plasma treated samples is obtained with FTIR. In Figure 8, the spectra of the

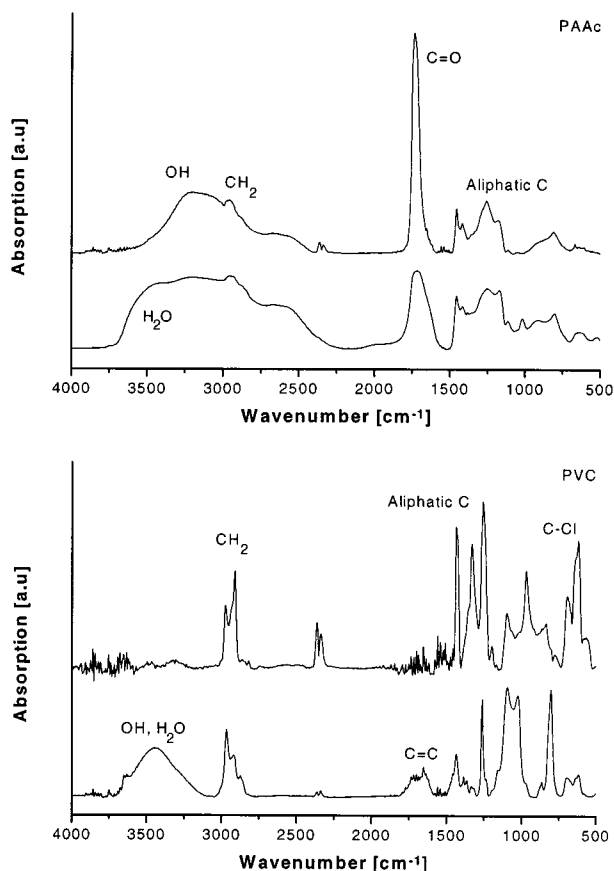


Figure 8. FTIR spectra of untreated (upper curve) and the insoluble fraction (lower curve, obtained by extraction, KBr pellet) of continuously argon plasma treated (300 s) PAAc (top) and PVC (bottom) samples.

insoluble fractions of argon plasma treated PAAc and PVC are compared with the spectra of the untreated polymers. The spectrum of the insoluble fraction of argon plasma treated PAAc is similar to that of the untreated polymer. The absorption band at 1740 cm^{-1} ($\text{C}=\text{O}$) is somewhat decreased in intensity. Furthermore, a broad absorption band around 3250 cm^{-1} is observed, which can be ascribed to both OH groups and water absorbed by the KBr. The possible formation of OH groups is in good agreement with the broadening of the main peak in the C 1s spectra (Figure 2, top). In the literature, an oxidation sequence for polyethylene is proposed^{1,24,25} in which, first, alcohol groups are formed that oxidize further to carbonyl and carboxylic acid groups. Eventually, these carboxylic acid groups are etched off of the surface. Therefore, the formation of OH groups, together with the resemblance of the FTIR spectra of pristine PAAc and the insoluble fraction of argon plasma treated PAAc, is also consistent with the proposed equilibrium between modification and ablation.

The spectrum of the insoluble fraction of argon plasma treated PVC is markedly different from the spectrum of the untreated polymer. The chloride absorption bands at 617 and 695 cm^{-1} have disappeared, and a new absorption band appears at 1600 cm^{-1} , which can be assigned to unsaturated bonds. Around 3400 cm^{-1} , a broad absorption band is observed, which is probably due to water absorbed by KBr. The changes in the $3000\text{--}2750\text{ cm}^{-1}$ region are the same as those in Figure 5. The small absorption band around 1700 cm^{-1} indicates that the insoluble fraction is only slightly oxidized. Considering the high oxygen content

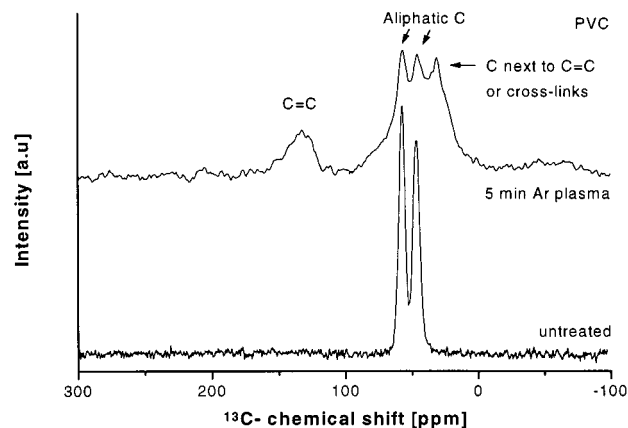


Figure 9. ^{13}C SSNMR spectra of untreated (lower curve) and the insoluble fraction (upper curve, obtained by extraction) of continuously argon plasma treated (300 s) PVC films.

measured with XPS (Figure 1, bottom), this implies that oxidation only takes place at the outermost top layer. This is in good agreement with the proposed cause for the observed oxidation.

^{13}C SSNMR is a valuable technique to detect unsaturated and aliphatic bonds. Therefore, the insoluble fraction of argon plasma treated PVC was characterized with SSNMR (Figure 9). In Figure 9, the signals of untreated PVC (46.8 and 57.1 ppm) are also visible in the spectrum of the insoluble fraction. Furthermore, two additional peaks can be observed. The peak around 130 ppm can be assigned to main-chain unsaturation. The peak at 30.7 ppm can be assigned to either carbon atoms incorporated in cross-links or carbon atoms next to unsaturated $\text{C}=\text{C}$ bonds. The oxidation found with XPS is not visible in the SSNMR spectra of the insoluble fraction of argon plasma treated PVC (absence of peaks between 200 and 250 ppm). It can therefore be concluded that only the outermost layer is oxidized. This is consistent with the proposed mechanism of oxidation.

The NMR technique used (CP-MAS) does not allow the calculation of absolute concentrations from the peak intensities. The low mobility of the system increases the intensity of signals coming from carbon atoms close to cross-links, whereas the reduced number of hydrogen atoms decreases the intensity of these signals because these structures have less protons than PVC. The latter effect is the most important. Taking these effects into account, the percentage of carbon atoms incorporated in unsaturated bonds was calculated to be at least 15%. This is higher than was found with derivatization XPS and is probably due to the oxidation of the outermost top layer which is measured with XPS.

Conclusions

Argon plasma treatment of vinyl polymers results in the introduction of unsaturated carbon-carbon bonds in combination with the formation of cross-links. A prerequisite for the introduction of unsaturated carbon-carbon bonds is that the pendant group is easily removed from the backbone and should be nonetching as a plasma component.

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