Surface Modification of Synthetic Polymers Using UV Photochemistry in the Presence of Reactive Vapours

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Summary: Polystyrene (PS), Polyurethane (PU), Polysulfone (PSU) and Polypropylene (PP) were surface modified using UV assisted treatment in the presence of acrylic acid (AA) vapour. In this context, PU and PSU were also modified using vapour of trimethoxy propyl silane (TMPSi). The surface changes were characterized by water contact angle measurement, Fourier transform infrared spectroscopy – Attenuated total reflection and X-ray photoelectron spectroscopy. Permanent hydrophilic surface was obtained by UV assisted treatment in the presence of AA vapour on all polymers studied. After 65 days of treatment, the polymer surfaces had the original degree of hydrophilicity as obtained immediately after treatment. By using vapour of TMPSi with UV radiation, the surface hydrophobicity of PU and PSU was increased after thermal treatment. The surface modification methodology used was simple and did not require any extensive set-up compared to traditional surface modification techniques.

Keywords: acrylic acid; photochemistry; polymers; surface modification; trimethoxy propyl silane; UV radiation

Introduction

Surface of pristine polymers tend to be chemically inert due to their low surface energy and for many applications, need to be modified to meet technical requirements. The chemical modification of polymer surfaces is of increasing importance in diverse aspects of modern technology and many research efforts are focused to change the surface properties of polymeric materials. For instance, surface modification of polyethylene[1] and polypropylene[2] using air plasma treatment was carried out to increase the adhesion property of the polymers. The best electrochemical properties of commercial polypropylene membrane were obtained by oxygen plasma etching followed by plasma polymerization coating of acrylic acid (AA).[3] Surface modification of polyurethane (PU) membrane using RF-plasma treatment with polymerizable AA vapour and non-polymerizable gases such as oxygen and nitrogen was carried out to modify and introduce specific functionalities on the PU surface.[4,5] Among various surface modification techniques that exists up to date, the most commonly used are corona discharge,[1] plasma,[6] plasma polymerization,[3,7,8] graft co-polymerization,[9] and ultraviolet(UV) / ozone treatment.[10] Among all surface modification technologies available, the use of UV radiation for modifying the surface is an easily applicable and economical method[11] in contrast to other techniques employing radiation and discharges. In the past decade, under the name of UV-induced, UV-assisted or UV-surface modification, several interesting applications were published. Successful UV-surface modification result was obtained in the attachment of amine and amide groups on the polystyrene surface by

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combined treatment of ozone aeration and UV illumination.[12] VUV light from excimer lamp was used to prepare a multifunctional silk fabric having hydrophobic and hydrophilic surface.[13] In addition, amine rich polyethylene surfaces were produced by using VUV irradiation through selection of excitation wavelength and gas.[14,15] Employing UV or VUV radiations with suitable reactive gas, it is possible to modify the surface of a polymer to hydrophilic or hydrophobic nature. The hydrophilic or hydrophobic surface is desirable for many industrial and biological applications like cell adhesion, printing, wettability of coatings, stain resistant textiles, antifouling paints, antisoiling architectural coatings and many more.

The use of AA and trimethoxy propyl silane (TMPSi) has special interests due to the chemical properties of those compounds. AA is a small monomer, can produce controlled polymerization reactions and recently it was used extensively in gas-phase plasma experiments[8] to modify the surface of different polymers like polypropylene,[16] polysulfone[17] and polyurethane.[7] Additionally, the molar ratio of carbonyl group in the whole molecule is high, which should enlarge the wettability of a surface.[17] Trialkoxysilanes (or silanes) have emerged as a very promising alternative for chromates in metal finishing industries[18] and photochemistry of trialkylsilanes was already used in UV assisted surface modification of polystyrene[10] to incorporate Si group on the polymer surface.

The motivation of the present work was to modify the surface properties of a polymer in a controllable and predictable way using a simple methodology: irradiation of the polymer surface by UV light in presence of a reactive atmosphere (AA or TMPSi). The surface modifications produced by the treatments were tracked by several surface sensitive techniques. A direct expression of the wettability of the surface is the contact angle of a water droplet on it.[19] The change in the surface hydrophilicity or hydrophobicity of the polymers by the treatment was characterized by measuring the water contact angle (WCA) as a function of UV irradiation time. The chemical changes produced on the surface after treatments were characterized by Fourier transform infrared spectroscopy – Attenuated Total Reflection (FTIR-ATR) and X-ray photoelectron spectroscopy (HR-XPS).

Experimental Part

Polysulfone (PSU) and polystyrene (PS) pellets were obtained from Aldrich Chemicals Co., UK. Polypropylene (PP) in granules form was obtained from Braskem, Brazil. Polyurethane (PU) (commercial name: Ellastolan PU1185A10) was obtained from BASF, Germany. AA and TMPSi were purchased from Aldrich Chemicals Co., UK and used as received. Nitrogen (99.99%) was obtained from White martins PRAXAIR INC, Brazil.

Polymer solutions of concentration $\sim 10^{-4}$ mol L^{-1} were prepared by dissolving the polymers in suitable solvents. PS and PSU solution were obtained by dissolving the polymers in chloroform. PU solution was prepared by dissolving PU in THF and PP solution was obtained by dissolution of PP granules in xylene at 125 °C under continuous stirring. Polymer films were prepared by spin-coating at 2000 rpm for 30 s from their solutions onto 10 mm × 10 mm stainless steel plates. Before film preparation, the stainless steel plates were washed ultrasonically in chloroform, hexane and isopropyl alcohol for 15 min each and then dried at room temperature.

The experimental setup for surface modification of polymers using medium pressure Hg lamp was explained in detail previously.[20] Briefly, vapour of AA or TMPSi was fed from a gas bubbler into a photochemical reactor through the inlet port of the reactor by using nitrogen as a carrier gas. The irradiated vapour gas mixture was exhaled through the outlet port. A constant flow of 4.5 cm^3/s of reactive vapour gas mixture was maintained throughout the irradiation. Surface modification of polymers with AA was carried out by keeping the gas bubbler containing AA at 50 °C. In the case of TMPSi treatment, the gas bubbler was kept at room temperature. Prior to all UV irradiation the reactor was purged for 15 minutes with the respective reactive vapour-nitrogen mixture to avoid any oxygen contamination. The irradiation was carried out for different time intervals and then the surface changes were characterized. In the case of TMPSi treated polymer films, before surface characterization, the films were introduced into an oven at ~ 90 °C for two hours to allow condensation reactions take place[18].

The modified and unmodified polymer surfaces were characterized by WCA measured by sessile drop method. The images of the water droplet were recorded at room temperature using a digital microscope (QX5) and contact angles were calculated using Surftens 3.0 version software. The WCA values reported were averages of six measurements performed in different areas of each sample surface. The changes in the chemical composition of modified polymer surfaces were examined using FTIR-ATR and XPS spectroscopy. FTIR-ATR spectra were obtained with spectral resolution of 4 cm^{-1} (Alpha-P model from Bruker). XPS data were obtained in a conventional electron spectrometer equipped with a hemispherical analyzer (7 channeltrons) and using Al Kα radiation as excitation source (Omicron, GmbH, Germany). The operation pressure in the ultra high vacuum chamber (UHV) during analysis was 10^{-7} Pa. Pass energy of 50 eV and 10 eV were used for survey and high resolution (HR-XPS) spectra respectively. The position of C 1s signal corresponding to C-C/C-H was used for energy calibration by setting the energy value at 285.0 eV. The XPS spectra were analyzed and peak-fitted after subtraction of a Shirley background using a Gaussian-Lorenzian peak shapes obtained from the CasaXPS software package.

Results and Discussion

UV-assisted Surface Modification of Polymers Using AA Vapour

WCA measurement of polymer films treated with UV radiation in the presence of AA vapour decreased when compared to pristine polymer films. Table 1 summarizes the WCA measured of untreated and treated polymers with an illumination time of 120 minutes. The WCA decreased with the increase in the irradiation time and reach a constant value for the all the polymers after 30-60 minutes of irradiation. PP, which is the most hydrophobic polymer used in our experiments becomes hydrophilic, after the surface modification with UV radiation in the presence of AA vapour. The other polymers PS, PU and PSU also shift to more hydrophilic, after the UV treatment. In addition, the AA treated polymer films were dipped in distilled water, agitated for 30 minutes at room temperature and then dried in air to confirm if the changes on the surface of polymer films induced by the treatments were permanent or not.[16] WCA remained unchanged before and after agitation in distilled water confirming a permanent surface modification of the film.

FTIR in ATR mode is very powerful technique to obtain chemical information on the top layers of a film. As a consequence, the chemical changes produced on the films by UV-treatment with reactive gases were studied using this technique. Spectra of all treated polymers with UV radiation in the presence of AA vapour confirmed the presence of carbonyl and hydroxyl groups on the surface of the films.

Table 1.
WCA of untreated and treated polymers with UV irradiation in the presence of AA vapour for a photolysis time of 120 minutes.

Sample	WCA of untreated polymers (degree)	WCA of treated polymers (degree)
Polystyrene	90 ± 2	28 ± 2
Polyurethane	85 ± 2	27 ± 2
Polysulfone	85 ± 2	22 ± 2
Polypropylene	99 ± 2	47 ± 2

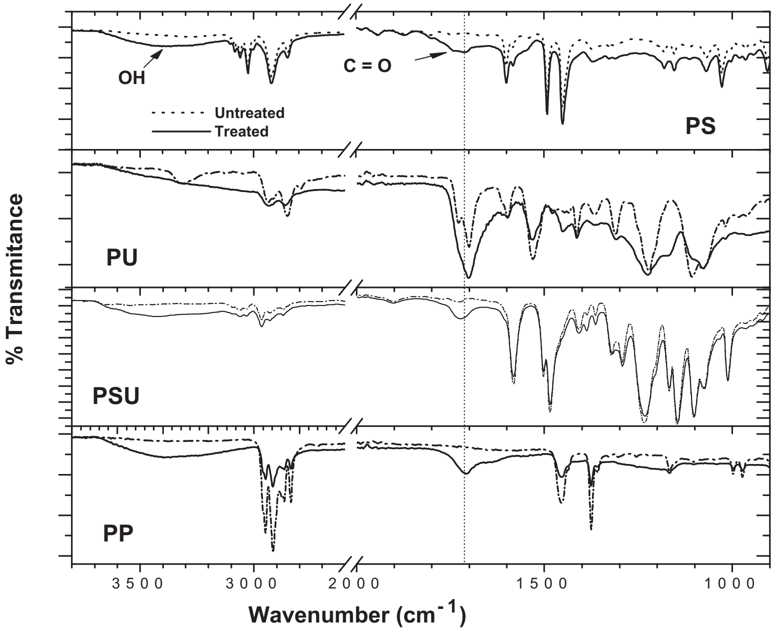

Figure 1.
FTIR-ATR spectra of untreated (solid line) and treated (dotted line) polymers with UV in presence of AA vapour. Photolysis time: 120 min.

Figure 1 shows the FTIR-ATR spectra of the untreated and the treated polymers. The broad band between 3700-2800 cm^{-1} is attributed to the hydroxyl, OH (dymer-polymer)[16] stretching vibrations and the sharp band at 1710 cm^{-1} corresponds to the carbonyl, C=O[17] stretching vibrations. Typical FTIR-ATR signals of treated polymers in Figure 1, reveals a common process of surface modification for all the polymers. The presence of electronegative group (carbonyl) and hydrophilic group (hydroxyl) on the treated polymer surface are responsible for the hydrophilicity and the decrease in the WCA of the modified polymers.

XPS wide scan spectra of untreated and treated polymer films were recorded to obtain elemental surface composition before and after the treatments. Table 2 summarizes the elemental composition of polymers surface calculated from the respective corrected areas of the XPS survey spectra (not shown). From Table 2, pristine PS and PP films which do not have any oxygen content before treatment have a high concentration of oxygen after surface modification with UV in the presence of AA vapour. In the case of PU and PSU, the oxygen contents increased after treatment when compared to the pristine polymer. In addition, Table 2 shows

Table 2.
Elemental composition (%) of C, N, O and S calculated from the XPS survey spectra of untreated and treated polymers with UV radiation in the presence of AA vapour.

Sample	Photolysis time (min)	Untreated				Treated			
		C 1s	N 1s	O 1s	S 2p	C 1s	N 1s	O 1s	S 2p
PS	60	99.5	–	0.5	–	70.6	–	29.4	–
PU [11]	60	88	2	10	–	84	0	16	–
PSU	60	83.7	–	10.6	5.7	72.3	–	26.4	1.3
PP	120	100	–	0	–	61	–	39	–

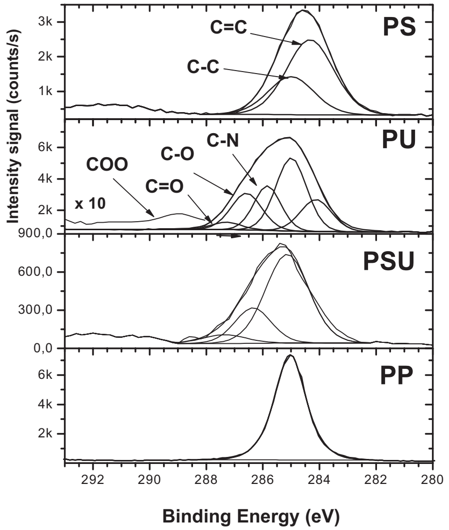

Figure 2.
C 1s HR-XPS spectra of untreated polymers.

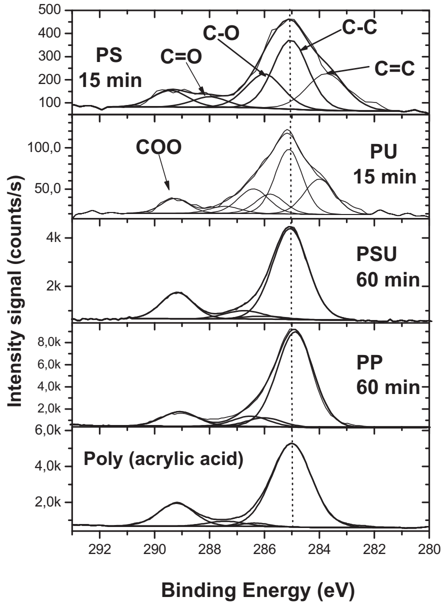

Figure 3.
C 1s HR-XPS spectra of treated polymers with UV radiation in presence of AA vapour. The irradiation time is indicated in the figure. C 1s HR-XPS spectra of PAA is shown as a reference at the bottom of the figure.

that the signals of N 1s (untreated PU) decreased to zero and the signal of S 2p (untreated PSU) decreased more than 75% respectively, after the treatment. Those results indicate that a thin film was formed during the UV treatment. XPS data supports WCA and FTIR-ATR information and quantitatively confirming the hydrophilic properties of the treated polymer surfaces.

HR-XPS spectra of unmodified and modified polymers surface with UV assisted treatment in the presence of AA vapour were obtained to know in more detail the chemical changes produced by the treatments. Figure 2 shows the C 1s XPS spectra of the untreated polymers and Fig. 3 shows the C 1s XPS spectra of the treated polymers. The changes produced in the C 1s envelope of all the polymers are evident when Fig. 2 is compared with Fig. 3. The increase in oxygen concentration are mainly due to new C=O and COO- linkages.[5,21] The introduction of electronegative groups in high concentrations at the polymer surfaces creates a hydrophilic surface on the treated films. When the photolysis time increased, the HR-XPS spectra remained without any important changes after 30 minutes of irradiation for all the treated polymers. After 30 minutes of irradiation all the C 1s HR-XPS spectra of the treated polymers looked similar to a typical C 1s HR-XPS spectrum of polyacrylic acid (PAA) (see Fig. 3, PSU-PP). The HR-XPS spectra at the bottom of Fig. 3 correspond to PAA thin film prepared in the laboratory. These results suggest the formation of a PAA like film on top of the treated polymers. The process of polymerization and formation of PAA film on different substrates by plasma treatments is a well know effect[17,22,23] and recently it was showed that similar reactions are also possible in UV treatment in presence of AA vapour.[11]

It is often observed that the properties imparted by surface modification treatments, change with time and this phenomenon are commonly called ageing. For example, it was found that the surface changes produced using the DC glow discharge air plasma on the surface of PP films were not permanent due to migration

Table 3.
WCA after 65 days of treatment with UV irradiation in presence of AA vapour for a photolysis time of 120 minutes.

Sample	WCA of freshly treated polymers (degree)	WCA of treated polymers after 65 days of ageing (degree)
Polystyrene	28 ± 2	25 ± 2
Polyurethane	27 ± 2	26 ± 2
Polysulfone	22 ± 2	24 ± 2
Polypropylene	47 ± 2	49 ± 2

Table 4.
WCA of untreated and treated PU and PSU films with UV assisted irradiation in the presence of TMPSi vapour and followed by heat treatment. Photolysis time is indicated in bracket.

Sample	WCA of untreated polymers (degree)	WCA of treated polymers (degree)
Polyurethane (120 min)	85 ± 2	96 ± 2
Polysulfone (60 min)	80 ± 2	97 ± 2

of polar groups into polymer bulk during ageing.[2] A major recovery by the PP surface was seen in the first 10 days of ageing, decreasing the surface energy with increasing WCA. On contrary, the formation of stable PAA-like layers on PP using plasma functionalization with AA was already reported by V.Sciarratta *et al.*[16] The effect of ageing on the changes imparted by the UV treatment in presence of AA was analysed by WCA measurement of the treated polymer films after 65 days of treatment. Table 3 shows WCA of freshly and aged treated polymers with UV radiation in the presence of AA vapour. The WCA remain unchanged even after 65 days of treatment. From the data in Table 3, the surface modification produced by UV assisted treatment in the presence of AA vapour on the polymer films is permanent within the experimental deviation and it does not vary during this time period.

UV-Assisted Surface Modification of Polymers Using TMPSi Vapour

PU, PS and TMPSi absorb UV photons from the Hg lamp and generation of radicals at the polymer surfaces or in the TMPSi gas phase are expected. Those complex radical processes would lead to grafting reactions. Photon energies at wavelength lower than 315 nm, is enough for the cleavage of Si-C and Si-O bonds of TMPSi.[10] Table 4 shows the WCA measured for untreated and treated PU and PSU films. After UV irradiation in the presence of TMPSi, the treated polymer samples were set at $\sim 90\,^{\circ}\mathrm{C}$ for two hours. This heating process increases the rate of the known condensation reactions typical for silanes compounds. As a result of UV treatment with TMPSi vapour and heating process, the WCA increased and resulted in more hydrophobic surface.

FTIR-ATR spectrum of PSU confirmed the introduction of Si groups at the polymer surface (see Fig. 4). Characteristic alkoxy-silyl and alkyl-silyl peaks appeared in the FTIR spectrum of treated PSU film. A strong band at 1010 cm-1 is attributed to the Si-O absorption and bands at 892 cm-1 and 1100 cm-1 corresponds to the SiOCH3 adsorption. The bands at 773, 818, 1216 and 1407 cm-1 confirms the addition of SiCH3

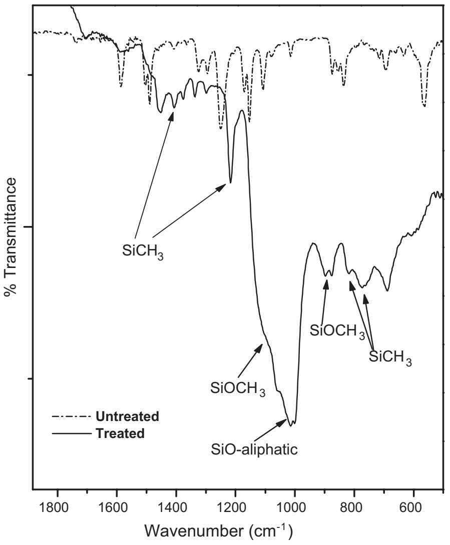

Figure 4.
FTIR-ATR spectrum of untreated and treated PSU film with UV radiation in presence of TMPSi vapour. Photolysis time: 60 minutes.

Table 5.
Elemental composition (%) of C, N, O, Si and S calculated from XPS survey spectra of untreated and treated PU and PSU films with UV radiation in the presence of TMPSi vapour and followed by heat treatment.

Sample	Untreated					Treated				
	C 1s	N	O	Si	S 2p	C	N	O	Si	S 2p
		1s	1s	2p		1s	1s	2p	2p	
PU	88	2.6	15.0	–	–	35	2.4	44.2	18.4	–
PSU	83.7	–	10.6	–	5.7	53	–	15	31	1

to the treated PSU films. Similar results were obtained for treated PU films.

To obtain quantitative information about chemical changes produced on the polymer surface after the UV irradiation in presence of TMPSi vapour, survey XPS spectra were recorded. The effect is exemplified for PU. Untreated PU showed weak Si signals belonging to the original polymer formulations (see top figure of Fig. 5). After UV irradiation in presence of TMPSi for 120 minutes, sharp XPS signals at 102.5 eV (Si 2p) and 152.0 eV (Si 2s) were easily detectable with high intensity (see bottom figure of Fig. 5). Quantitative data presented in Table 5 shows the increasing amounts of Si and O at the polymer surface after treatments. The increase in the oxygen signal and corresponding decrease in the carbon signal are additional evidences for the TMPSi treatment because the treatment was carried out in nitrogen gas atmosphere.

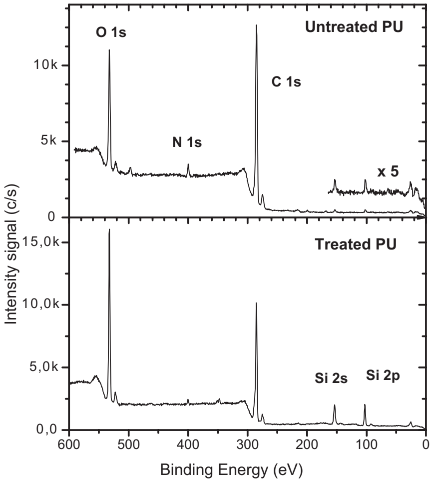

Figure 5.
XPS survey spectra of untreated and treated PU films with UV radiation in presence of TMPSi vapour. Photolysis time: 120 minutes.

Conclusion

The surfaces of the four polymer thin films studied were treated by UV irradiation in the presence of AA or TMPSi vapour. The treated polymer film surfaces were modified to hydrophilic or hydrophobic when the vapour of AA or TMPSi was used respectively. UV-assisted treatment in presence of AA vapour produced a PAA like film on top of the treated polymers independent of the polymers used. These results suggest that AA polymerization reactions occur during illumination that is commonly observed in low pressure plasma experiments. The hydrophilicity obtained by the UV modification in presence of AA vapour remained intact even after 65 days of treatment. A more hydrophobic surface of PU and PSU with incorporation of Si group on the polymer surface was obtained when using UV radiation in presence of TMPSi vapour followed by heating process. The methodology used here is simple and it does not need any extensive set-up compared to other surface modification techniques.

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