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Permanent hydrophilic modification of polypropylene and poly(vinyl alcohol) films by vacuum ultraviolet radiation

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ABSTRACT

Polypropylene (PP) and Poly(vinyl alcohol) (PVA) both synthetics polymers but one of them biodegradable, were surface modified by vacuum ultraviolet (VUV) irradiation. After VUV irradiation in an inert nitrogen atmosphere, the films were exposed to oxygen gas. The treated films were characterized by water contact angle measurements (WCA), optical profilometry, FTIR-ATR, XPS, UPS and NEXAFS techniques. PP and PVA VUV-treated films reached superhydrophilic conditions (WCAs <10°) in about 30 min of irradiation under our experimental conditions. It was observed that when the WCAs reached about 35–40° the hydrophilicity was permanent in both polymers. These results contrasted with typical plasma treatments were a rapid hydrophobic recovery with aging time is usually observed. UPS and XPS data showed the presence of new functionalities on the PP and PVA surfaces that were assigned to COO, C$=$O, C$-$O and C$=$C functional groups. Finally, grafting of styrene (ST) as a typical monomer was tested on PP films. It was confirmed that only in the VUV irradiated region an efficient grafting of ST or polymerized ST was found. Outside the irradiated regions no ST grafted was observed. Our results showed the potential use of VUV treatment for surface modification and processing of polymers which lack chromophores in the UV region.

1. Introduction

Polypropylene (PP) is a commodity and thermoplastic polymer widely used in the industry and daily life. PP shows excellent mechanical properties and a high adaptability to complicated structures and in consequence it is used in a broad range of applications. However, this polymer has important disadvantages in the fields of coatings, printings, paints and metallization because PP has low wettability due to its hydrophobic surface properties [1]. For this reason PP films need enhancement of the wettability and adhesive properties and therefore additional treatments are required to increase the surface free energy.

Recently the use of polymers, such us PP has been a matter of concern in relation to environmental problems associated with synthetic polymers pollution and efforts have been carried out to find mechanisms to degrade those types of plastics [2]. On the contrary, Poly(vinyl alcohol) (PVA) is a biodegradable synthetic polymer, relatively harmless [3] and it is used in packaging applications, agriculture and a wide range of industrial fields due to its excellent mechanical and optical properties. PVA has also been used as a biomaterial in tissue engineering applications [4,5]. However, some aspects must be enhanced in PVA, such as the high cost of synthesis and low biodegradation rate [6]. PVA and similar biodegradable polymers present in many cases relatively low surface free energy which will determine low cellular adhesion and degradation rates [7–9].

PP and PVA lack of a UV chromophere and a simple UV photochemical treatment cannot be used. The surface properties of synthetic and biodegradable polymer are usually modified by different techniques, such as: plasma treatment [1,10,11], plasma polymerization [12–14], corona-discharge [15], grafting [16], graft co-polymerization [17] and nuclear radiation [18,19]. Dry techniques as low power radio-frequency (RF)-plasma treatments have been extensively used to improve the surface properties of polymer materials. The extensive set up used in plasma techniques, which employ radiation and discharges, and the regression to the almost untreated state after the treatments are the main disadvantage of those techniques [20]. A polyolefin like PP treated with plasma sources have shown rapid hydrophobic recovery with aging time in a few days or weeks [10,21–25]. Detailed studies about the aging mechanisms that originate the hydrophobic recoveries in plasma or Vacuum Ultraviolet (VUV) treatments of several common polymers have carried out in the past [21,22,26]. Those investigation have concluded that the main mechanisms of aging are adsorption of low-energy contaminants from the atmosphere, outward diffusion of light oligomers or additives, inward-diffusion of low molecular weight oxidized species and reorientation of side chains or pendant groups on the macromolecules. Interesting results by Rutherford Back Scattering experiments of Argon plasma treated PP showed that oxygen was observed up to the depth of about 60 nm with the oxygen concentration decreasing from the surface to the bulk. But nevertheless the power of the plasma discharge used, the full contact angle restoration was achieved after about 3 days of aging [10]. Recently, a series of studies suggested that the hydrophobic recovery after plasma treatment is due to di-

pole–dipole interactions of treated polymer with molecules of the nearby medium [27]. Those mechanisms may combine to produce a hydrophobic recovery in PP and other polymers adding cost in the production line.

The use of UV light as a simple, dry and economic excitation source has showed in many cases similar results to plasma treatments [28–31]. PP and PVA films are transparent to UV light or absorb weakly if especial additives are added. Therefore UV treatment cannot be use efficiently to modify the surface of polymers that lack of UV chromophores. In this sense VUV radiation appears as an interesting alternative to plasma treatments due to the simple set up and control of the experimental parameters. Most plasmas are emitters of photons in the UV and VUV and automatically include a fraction of UV and VUV-induced contribution to the final outcome [32]. VUV photons have high energies (6–12 eV) well in excess of those of covalent bonds in most polymers given rise to complex photochemical processes [33,34]. After VUV treatment of the surface of the pristine polymer, grafting reactions can be carried out easily to modify permanently the surface properties of the polymer film to meet specific technical requirements.

In the present contribution we report the surface treatment of PP and PVA films using VUV light of 162 nm to induce permanent hydrophilic properties to the film surfaces. Additionally, grafting reactions of styrene on PP treated surfaces were carried out. Water Contact Angle (WCA) measurements, Fourier Transformed Infrared Spectroscopy in Attenuated Total Reflectance mode (FTIR-ATR), X-ray Photoelectron Spectroscopy (XPS), Near-edge X-ray Absorption Fine Structure (NEXAFS), Ultraviolet Photoelectron Spectroscopy (UPS) and Optical Profilometer measurements were used for the characterization of the chemical structure of the treated PP and PVA films.

2. Experimental

2.1. Materials

Styrene was supply by Sigma with 99% of purity. Toluene 99.9% and isopropyl alcohol 99.9% were obtained from Merck (Brazil). Nitrogen (N_2), 99.99% was obtained from White Martins PRAXAIR INC and used as received.

Two types of Polypropylene (PP) films were used in the present work. High melt flow rate PP homopolymer designed for injection moulding and fiber extrusion (BRASKEM-H 301, 0.905 g/cm^3 density and 10 g/10 min melt flow) were processed by injection molding, cleaned in ultrasonic bath with acetone for 30 min, dried at room temperature and then stored in a desiccator. The final PP substrates were about 30×10 mm^2 size and 3 mm thickness. Alternatively, commercial PP films supplied by Converflex Argentina SA, biaxially-oriented and 60 μm thick modified previously by corona treatment (42 dyn/cm^2) on one side were also used. The PP films were cut into 5 cm × 5 cm sections for VUV treatment. Before the VUV treatment, the films were washed ultrasonically in acetone and distilled water for 15 min and then dried at room temperature.

Poly(vinyl alcohol) (PVA), obtained from Sigma Aldrich (Mw = 130,000 g/mol), was dissolved in deionized water (10^{-4} mol/L) at 80 °C and kept under mechanical agitation until complete dissolution. The films were prepared by two techniques: spin coating and casting. The solution at 80 °C was used to prepare films by spin coating in heated polished stainless steel substrate (1 cm × 1 cm) at 70 °C. The casting film was prepared on Teflon plate at room temperature overnight. After that the films were dried at vacuum oven during 24 h. The spin coating films were only used when synchrotron

radiation was the excitation source. The thickness of the spin coated and casted films was between 200 and 400 nm and (29 ± 4) μm respectively.

2.2. Water contact angle measurements

The wettability was measured by the sessile drop method where 2 μL drops of deionized water were gently deposited on the surface at room temperature using a microsyringe. The images were captured using the "Drop Shape Analysis System" equipment, Kruss DSA. All the measurements were repeated at least three times in different positions. The images were captured using a digital video camera and analyzed for contact angle measurements using Surftens 3.0 software. WCAs measurements were carried out after about 15 min of the VUV treatments.

2.3. Fourier transformed infrared spectroscopy (attenuated total reflectance mode)

Fourier transformed infrared spectroscopy measurements (FTIR) were performed using an Alpha-P model, Bruker, with a spectral resolution of 4 cm^{-1} and 24 scans. The method of Attenuated Total Reflectance (ATR) with diamond prism was employed at an incidence angle of 45°.

2.4. X-ray photoelectron spectroscopy (XPS)

XPS spectra were obtained in a conventional electron spectrometer (Omicron) equipped with a high performance hemispherical energy analyzer with a seven-channeltron detector and using Al Kα radiation as the excitation source. Survey spectra were recorded with pass energy of 50 eV, whereas selected atomic signals were acquired with 10 eV of pass energy. In the spectra, the position of the C—C/C—H was specified, and other peaks of different carbon environments were fixed relative to this peak, set at 285.0 eV. The angle between the analyzer and the substrate normal was kept constant at 45°. The C 1s envelope was analyzed and peak-fitted after subtraction of a Shirley background using Gaussian-Lorenzian peak shapes obtained from the CasaXPS software package.

2.5. Near edge X-ray absorption fine structure (NEXAFS) and ultraviolet photoelectron spectroscopy (UPS)

NEXAFS and UPS experiments were carried out at the Brazilian Synchrotron Light Source (LNLS), Campinas, Brazil. The SGM (Spherical Grating Monochromator) beam line, for ultraviolet and soft X-ray spectroscopy (250–1000 eV), which gives a spectral resolution (E/ΔE) better than 2000, was used as the monochromatic photon source for NEXAFS measurements. NEXAFS spectra were obtained by measuring the total electron yield (electron current at the sample) simultaneously with a photon flux monitor (Au grid). The final data were normalized by this flux spectrum to correct for fluctuations in beam intensity. UPS spectra were obtained at the TGM (Toroidal Grating Monochromator) beam line which covers a photon energy range from 12 to 310 eV. For particular photodegradation tests, the films were irradiated by synchrotron radiation (SR) during a fix period of time under UHV conditions. Broadband SR (zero-order light from the beamline) was used for the polymer degradation. After irradiation, one atmosphere of oxygen was introduced into the UHV chamber for 30 min following a methodology already utilized in previous studies [35–38]. UPS spectra were obtained at the photon energy of 150 eV before and after the treatments.

The experimental set ups include a XYZ sample manipulator housed in an ultra high vacuum (UHV) chamber with a base pressure of 10^{-7} Pa. The substrates were directly attached to the sample holder by using conducting double sided tape. The synchrotron beams were slightly defocused to avoid or minimized sample charging during acquisition.

2.6. Optical profilometer measurements

Surface roughness measurements were carried out using an optical profilometer, Contour GTK 3D Optical Profiler. The software "Vision64" was used for data analyze and the root mean squared roughness (RMS) was calculated. Each value corresponds to an average of 5 measurements at four different positions of the surface.

2.7. Vacuum ultraviolet (VUV) treatments

VUV irradiation was carried out by a Deuterium almost monochromatic source (162 nm) of 140 W from Hamamatsu, Japan. The irradiations were performed in a homemade stainless steel reactor fitted with the excitation source. A scheme of the apparatus is shown in Fig. S1 in Supporting information. During irradiation a constant flow of inert nitrogen atmosphere at 5 mL/s enter the photochemical reactor. When it was necessary a reactive gas, such as oxygen was introduced after the irradiation period. The distance between the samples and the source was kept constant in 2.5 cm (see Fig. S1 in Supporting information). The substrates were directly fixed to the sample holder that was situated in front of the Lamp.

2.8. Styrene grafting

For the styrene grafting experiments commercial atactic PP films of 60 μm thickness and injection moulding PP sticks of 2 mm thickness were used. The commercial films were received with a previous corona treatment (see Section 2.1) and were slightly hydrophilic (WCA = 89°). The VUV irradiated PP films were exposed to air for 1 min and after about 5 min they were immersed 30 min in the styrene monomer, which had been previously bubbled in dry nitrogen. Finally, the films were washed in toluene and isopropyl alcohol and dry before characterization.

3. Results and discussion

3.1. Polypropylene VUV treatments

Untreated PP sticks showed a WCA of (106 ± 3) degrees. When these substrates were treated by VUV photons (in an inert N_2 atmosphere) and oxygen gas was introduced into the chamber after the photochemical treatment, the WCA decreased quickly to reach almost a superhydrophilic condition (see inset of Fig. 1). At irradiation times equal or higher than 30 min, an approximately constant WCA of 10° was obtained. Aging measurements showed that the hydrophobic recovery of the VUV treated films was very low and the films stabilized in a permanent hydrophilic condition of about 40° for several months. Fig. 1 shows the dependence of the WCA on aging. PP treated samples retained their hydrophilic surface properties even after 12 months of the treatments that was the last measurement carried out. This result is very difficult to obtain using traditional techniques such as plasma treatment, where the surface recovers the hydrophobic properties within a few hours or days after the treatments [21–23,39]. The rapid hydrophilic conversion of the surface wettability of the PP samples is a known effect already observed under γ
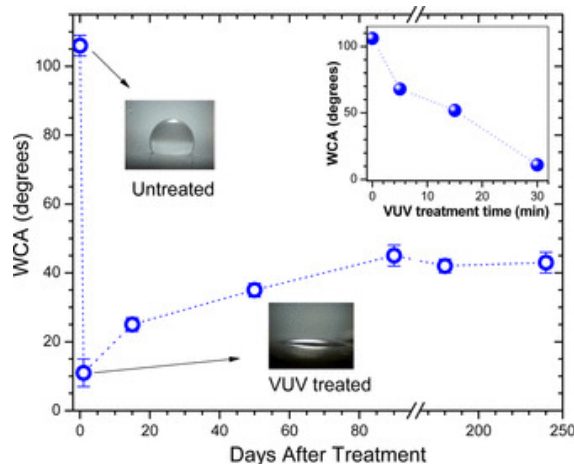

Fig. 1. WCA dependence on the aging time for PP treated substrates with VUV light for 30 min. VUV treatment was carried out in an inert N_2 atmosphere and after irradiation oxygen gas was introduced into the chamber without VUV illumination. Inset: dependence of the WCA on the VUV irradiation time.

and plasma sources due to the presence of labile methyl side groups [25].

It is known that the VUV photons' penetration depth (a few tens of nm) depends on the polymer's chemical structure and in particular on the excitation wavelength and intensity [34,40]. Previous studies [40] have already observed in their detailed study of several hydrocarbon polymers that VUV radiation lead to scission reactions that resulted in the formation of volatile fragments, such as hydrogen and light hydrocarbons. These fragments can also react to form C=C bonds or cross-link with the new created free radicals in the polymer back-bond rendering the surface-near modified region more rigid and resistant to ablation. Those processes are the source of so-called aging where the concentration of chemically-bonded oxygen resulting from VUV exposure increase with irradiation and exposure to the ambient atmosphere.

The chemical state of the VUV-irradiated surfaces was examined in more detail using FTIR-ATR and XPS measurements. FTIR-ATR analysis of treated PP films by VUV (See Fig. S2 in Supporting information) showed that after 30 min of VUV irradiation new bands appeared in the spectrum. A broad band located between 3600 and 3100 cm^{-1} is characteristics of the hydroxyl groups stretching (—OH) [41] and a peak at about 1720 cm^{-1} can be assigned to stretching of carbonyl groups (C=O) [41]. Both main signals show the effect of the VUV irradiation and oxidation of the PP film surface. More surface sensitive chemical information of the changes produced by the VUV treatments on the surface region of the PP films was obtained by XPS analyses. Untreated PP films showed almost not oxygen content at the surface with only the presence of some atmospheric contamination. When the PP films were irradiated for 30 min and then expose to air, the O/C signal ratio increased from about 0.01% for a pristine PP film to 0.13% (See Fig. S3 in Supporting information). The increase in the oxygen content on the polymer surface after irradiation showed the extent of surface oxidation by the combination of VUV light and exposure to the oxygen atmosphere.

New functionalities in the polymer surface were observed after the VUV treatments. Peak-fitting of the C1s XPS spectrum of a PP film without treatment (Fig. 2a) shows only the typical PP contributions of C—C/C—H bonds with a very simetric peak. After
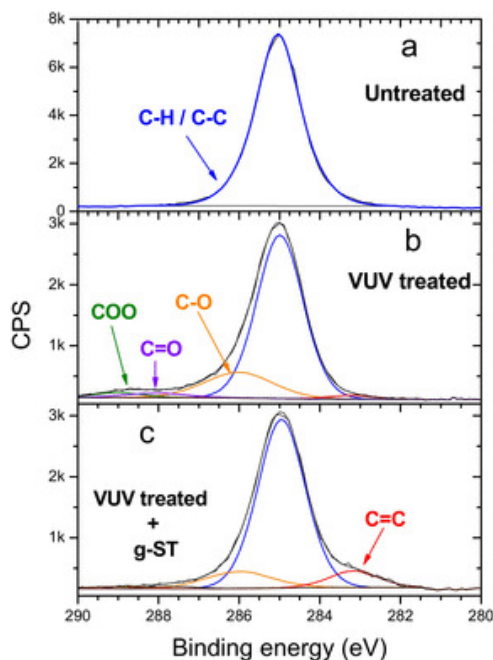
Fig. 2. C 1s XPS core-level spectra of PP samples untreated (a) and treated with VUV irradiation for 30 min in N$_2$ atmosphere (b). After irradiation the PP films were exposure to air. Finally, after VUV treatment styrene was grafted on the PP substrates only in the irradiated area (c) (see Section 3.2 for details).

VUV irradiation and air exposure (Fig. 2b), the C1s signal showed the appearance of contributions of photoelectrons related to new functionalities present on the PP surface that can be assigned to COO (289 eV), C$=$O (288 eV), C$-$O (286 eV) and C$=$C (283.5 eV) in minor amounts [31,41].

3.2. Styrene grafting

In the last decades the use of surface modification techniques became essentials to change the surface properties of polymeric materials according to tailor-made specifications designed for target applications. One of the usual ways to modify polymers properties is grafting, which is a method wherein monomers are covalently linked onto the polymer chain. In Section 3.1 it was shown that the surface of PP films was converted to a permanent hydrophilic state after the VUV treatments. To test the efficiency of grafting using VUV irradiation and later exposure to oxygen atmosphere or air, injection molding and commercial PP substrates were used. Commercial PP films were received with a previous corona treatment and a per-

manent hydrophobic character. Both types of films were irradiated using a mask, where the irradiation area corresponded to the central region (a) in Fig. 3i. After treatment with VUV light and oxygen exposure, the PP samples were immersed in styrene (ST) monomer. The irradiated and non-irradiated areas were in contact with ST monomer for 30 min.

Table 1 resumes the WCA measurements after the ST grafting tests. As can be seen from the results presented in Table 1, efficient grafting of ST was only observed in the VUV irradiated area (region (a) in Fig. 3i) where a hydrophobic WCA of about 120–123° was measured (see Fig. 3iv and Table 1). Outside the irradiated area (region (b) in Fig. 3i) there was not grafting of ST because the WCA measured corresponded to the same value of the untreated PP films (see Fig. 3ii and Table 1). The results confirmed an efficient mechanism of grafting only in the hydrophilic irradiated area (Fig. 3iii and Table 1) where the VUV treatment (irradiation plus contact with an oxidant atmosphere of oxygen) generated reactive species on the surface that finally reacted with the ST monomers.

To confirm the presence of ST grafted on the treated PP surface, FTIR-ATR, XPS and NEXAFS spectroscopy were used. Due to the grafted film formed on top of the PP treated substrates was very thin, or at least thin enough for the FTIR-ATR technique, any signal of C$=$C bonds was clearly obtained (result not shown). Therefore, a much more surface sensitive technique than FTIR-ATR, such as XPS was used. XPS survey data showed that the O/C ratio change from 0.086 to 0.15 when the PP is treated with VUV light and return to a value close to the untreated O/C ratio of 0.10 when ST monomers are grafted on the surface (see Table S1 in the Supporting information for more details). Interesting, the grafted film shows a slightly higher concentration of carbon and lower concentration of oxygen than the VUV treated film, indicating that a thin layer of a different chemical composition is on top of the VUV treated PP films. Peak-fitting of the C1s XPS spectra of a PP film without and with treatment showed the contributions of a high C$=$C signal in the ST grafted film (see Fig. 2-bottom). This result indicated the presence of ST monomers or polymerized ST on the PP surface. Additionally, after grafting of ST monomers on the VUV PP films the contributions of electrons related to COO groups almost disappeared and the C$=$O signal strongly decreased confirming the changes on the surface after ST grafting.

In order to corroborate the presence of ST monomers or probably a ST polymerized film on the VUV treated PP surface, NEXAFS analyses were carried out. NEXAFS spectroscopy is a powerful surface sensitive technique to identify and distinguish electronic transitions of molecular groups in different chemical environment [42,43]. Fig. 4 shows a typical NEXAFS spectrum of untreated commercial PP film where it is possible to assign the following contributions to the total spectrum: C1s → σ*$_{C-H}$ (287.0 eV) and C 1s → σ*$_{C-C}$ (291.7 eV) [44,45]. When the commercial PP films were grafted with ST the spectrum changed slightly the shape with the appearance of a new peak localized at 284.8 eV (see inset of Fig. 4). That signal is a typical transition from a core C 1s to a p*$_{C=C}$ bond. The C 1s → π*$_{C=C}$ resonance at 284.8 eV observed in the ST

Fig. 3. Styrene grafting in commercial PP films untreated and treated with VUV radiation for 30 min in an inert N$_2$ atmosphere. After photolysis the irradiated samples were exposed to pure oxygen. (i) Scheme of the mask use for the experiments where (a) corresponded to the irradiated area and (b) to the area without irradiation; (ii) commercial PP film without VUV irradiation; (iii) commercial PP film with 30 min of VUV irradiation; (iv) idem (iii) plus grafting with styrene.

Table 1
WCA measurements of untreated injection molding and commercial PP films treated with VUV for 30 min and immersed in styrene (ST) monomer.

Sample	Area of analyses (see Fig. 3-i)	WCA (degrees)	
		Commercial PP films	Injection molding PP substrates
Untreated	–	89 ± 2	102 ± 4
VUV treated	a	69 ± 2	~11
VUV + ST	a	120 ± 1	123 ± 1
VUV + ST	b	89 ± 1	100 ± 2
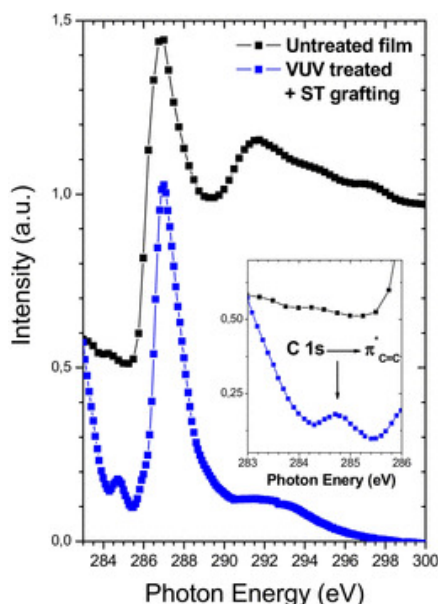
Fig. 4. The carbon *K*-edge NEXAFS spectra of untreated and grafted-VUV treated commercial PP films. VUV irradiation time: 30 min. After photolysis the irradiated samples were exposed to pure oxygen and finally immersed in the ST monomer for 30 min. VUV irradiation was carried out in an inert N$_2$ atmosphere.

grafted films (Fig. 4) matched exactly the value obtained in experiments of plasma-polymerized styrene films obtained by the appropriate choice of external plasma parameters, such as duty cycle, power and monomer pressure [46]. The results obtained by NEXAFS spectroscopy confirm the efficient grafting of ST monomers only on the VUV irradiated area of the commercial PP films.

3.3. Poly(vinylalcohol) VUV treatments

PVA was also exposed to VUV irradiation in an inert atmosphere of nitrogen. After the photolysis of the films, oxygen was introduced into the chamber during 15 min to oxidize the irradiated surface. A Pristine PVA film has a WCA of 54 ± 2°. WCA of the irradiated films showed a continuous decrease when the VUV exposure time increased. For example, for the VUV irradiation times of 10 and 20 min the measured WCAs were 42 ± 2° and 14 ± 1° respectively. Furthermore, it was possible to observe that after 30 min of irradiation

the PVA surface changed from hydrophilic to superhydrophilic reaching WCAs lower than 10°.

Changes in chemical surface composition of PVA films treated with VUV light were investigated by FTIR-ATR and UPS spectroscopy. Fig. 3 shows the FTIR-ATR spectra of pristine and VUV treated PVA films. The main feature observed in Fig. 5 is the merge of an intense signal at 1703 that can be assigned to the carbonyl stretching of C=O in aliphatic ketones (1725–1700 cm^{-1}) [41]. These results show the insertion of oxygenated functionalities after treatments of the PVA films (VUV and later introduction of oxygen).

Thin films of PVA were also irradiated with a wide VUV range using the zero-order light from the TGM SR beam line to know details about the photodegradation mechanism and changes in functionalities that occur after irradiation. The UPS spectra of untreated PVA shown in Fig. 6-top reveals good agreements with published spectroscopy data on polyethylene after VUV treatments with a contribution of C—O functional group [47,48]. The main signals can be assigned as follows: the first broad peak located at 4–11 eV mainly involve the orbitals of the C—H and C—C (C 2p) bonds. The characteristic band located at 12–25 eV is associated mainly with the carbon 2s orbitals from the polymer main chain. After irradiation and exposure to oxygen atmosphere the UPS spectra of the PVA film changed rapidly with the increase in the irradiation time. At 1 min of irradiation a distinctive shoulder at 3.5-3.8 eV evidences the presence of new C=C bonds in the polymer chain [47,48]. Fig. 6 shows that at 5 min of irradiation the shoulder seems to decrease slightly and after 15 min of continuous irradiation the C=C contribution complete disappeared. The broad peak located at about 8 eV and extending up to 14 eV can be associated to C=O and COO groups grafted on the surface after the treatments in analogy with the results obtained in the photodegradation study of poly(methyl methacrylate) (PMMA) by VUV photons [47]. The grafting of new polar group in the surface region is the origin of the hydrophilicity observed after VUV modification of the PVA films.

The WCAs data shows that the hidrophilicity of the treated PVA films increased when the VUV irradiation time at 162 nm increased, reaching a superhydrophilic state at 30 min of irradiation. In spite FTIR-ATR and UPS data (see Figs. 5 and 6, respectively) show a clear presence of hydrophilic groups on the surface; the fact that the
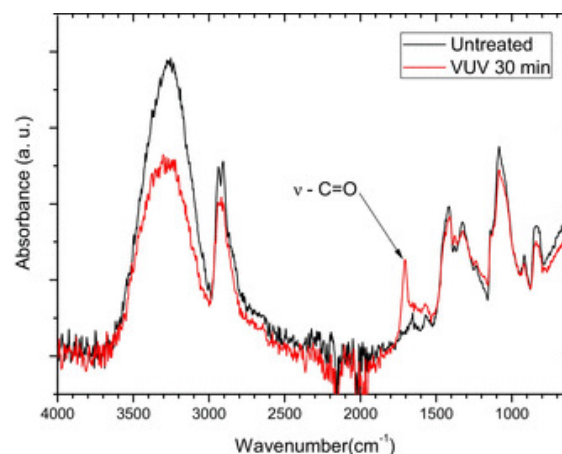

Fig. 5. FTIR-ATR spectra of pristine and VUV treated PVA films. Irradiation time: 30 min. After the irradiation the films were exposure to an oxygen atmosphere for 15 min.
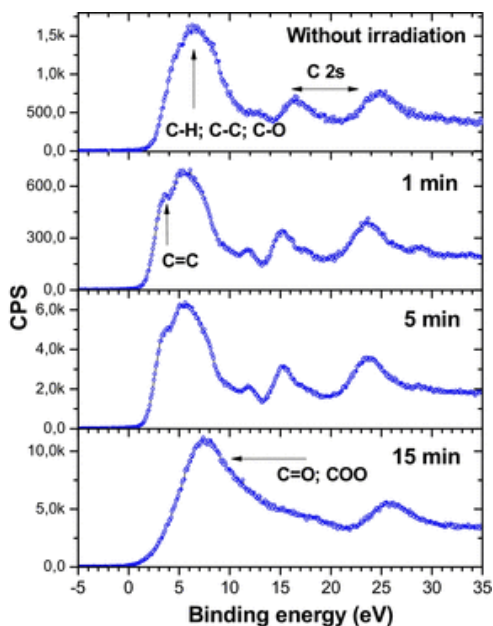
Fig. 6. Photodegradation of PVA films measured by UPS. Zero order light from the SR beam line was used to degrade the polymer. After each irradiation time 1 atm of pure oxygen was introduced in the UHV chamber to oxidize the irradiated films. Excitation energy: 150 eV.

treated surface with 30 min of irradiation reached a state of total wettability means that additional effects of surface capillarity may exist. To get insight into the morphology of the surface before and after the VUV treatments profilometry measurements were carried out and the results are presented in Fig. 7. The typical surface roughness of the

non-irradiated areas ($\sim$1.2 mm^2 scanned area), was 89 ± 5 μm. Fig. 7a shows a quite homogenous roughness of the untreated PVA film. Following exposure with VUV light and oxygen the surface morphology of PVA changed significantly and distinct self assembled like channels, of 50–70 μm were formed over the illuminated area (see Fig. 7b). The roughness of the irradiated region decreased (RMS = 59 ± 9 μm) compared to the pristine PVA surface with an even larger decrease in roughness for the top regions of the structures.

Previous independent studies using 157 nm laser radiation suggested that important morphological changes on the surface of PMMA films formed by spin coating on Si wafers were induced with increasing the number of VUV laser pulses [49,50]. In those works it was observed that the surface morphology indicates a high degree of organization and that the surface area (porosity) of the polymeric material increases as the laser dose increased. A detailed report on the PMMA film thickness dependence on the absorption and desorption of water at different vapor pressures for the non-irradiated and irradiated samples showed the importance of the water absorption during the process [50]. The absorption of water molecules within the polymer film was responsible for film thickness increase compared to the non-irradiated samples, concluding that the higher swelling was due to surface chemical modification and porosity increment following laser treatment. Similar arguments can be used for our experiments where we have observed significant changes in surface chemical composition with incorporation of polar groups and large morphological changes after the VUV treatments. The combination of morphology and surface chemistry led to the observed superhydrophilic results found at long VUV irradiation times.

Finally an aging study was carried out on PVA films treated with VUV light. It was observed that VUV treated PVA films resisted the recovery of the original wettability. During the first month the WCA of the treated films remained highly hydrophilic (WCA <15 °) reaching after 50 days a constant value of about 35° (see Fig. S4 in the Supporting information). In a similar way that it was observed for
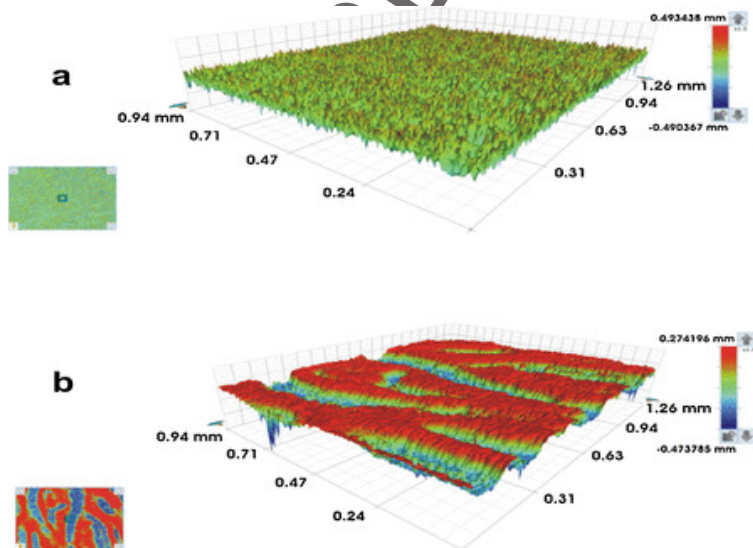

Fig. 7. Profilometry images of PVA films before (a) and after VUV irradiation (b). Irradiation time: 30 min. RMS: 89 ± 5 μm (a) and 59 ± 9 μm (b).

PP films (see Fig. 1), VUV treatment of PVA films retained a high degree of hydrophilicity during several months after the treatments.

4. Conclusions

A synthetic (PP) and a biodegradable polymer (PVA) without UV chromophores, were efficiently surface modified by a combination of VUV electromagnetic irradiation with exposure after irradiation in an oxygen atmosphere. Using a combination of WCA, optical profilometry, FTIR-ATR, XPS, UPS and NEXAFS techniques a detailed characterization of the chemical effects of the VUV radiation in PP and PVA films was obtained. PP and PVA films treated with VUV for 30 min reached superhydrophilic conditions (WCA <10°). Differently to what it is usually observed in typical plasma treatments of polymers, it was confirmed that the changes produced by VUV irradiation on the PP and PVA films resisted aging for very long periods of time. Additionally, it was shown in commercial and injection moulding PP films that the surface chemical modification and morphological changes produced by the VUV treatments led to an efficient styrene grafting mechanism. The grafting was only observed in the irradiated region of the PP films.

The obtained results also showed the potential of the VUV treatments that would allow the processing of a polymer surface in industrial applications at later stages. The obtained results that showed that no hydrophobic recovering of the treated surfaces in months after the treatments would be of great interest for the industry. Furthermore, implementation of the process at industrial scale does not require great economical investments and the process can be easily carried as a pre-treatment operation.

Aknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apsusc.2016.04.091.

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