

Multiple hydrophilic polymer ultra-thin layers covalently anchored to polyethylene films

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ABSTRACT

A novel procedure has been developed to covalently graft multiple hydrophilic polymer ultra-thin layers to functionalized polyethylene surface. Polyethylene films have been functionalized by two methods, chromic acid oxidation and maleic anhydride grafting, to produce surfaces containing reactive groups, carboxylic acid and anhydride, respectively. The reactive groups formed in the functionalization were used to anchor a poly(vinyl alcohol) (PVA) ultra-thin layer by thermal esterification. After anchoring PVA, a second ultra-thin layer, constituted of poly(acrylic acid) (PAA), was also anchored. The second layer was anchored by thermal esterification between PVA hydroxyl groups and PAA carboxylic acid groups. The procedure presented in this work allows the formation of an ultra-thin layer. The macromolecule anchoring reactions occur only at the interfaces, consequently, only the macromolecules in contact with the interface are anchored. The formation of the ultra-thin layer and the surface characteristics have been analyzed through XPS, ATR-FTIR, SEM, and AFM data.

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1. Introduction

Ultra-thin anchored polymer layers have been utilized to improve the performance of solid materials. Anchoring polymers to solid surfaces may afford the control of many properties such as adhesion, wettability, friction, adsorption, permeability, catalyst immobilization, and biocompatibility [1–3]. These properties are very important for many technologies. The several polymer layer anchoring techniques described in the literature may be subdivided into two main kinds, “grafting-to” (polymer attachment to the solid surface) and “grafting-from” (polymerization initiated from solid surfaces) [4–6].

Anchored polymer ultra-thin layers afford permanent surface modification through covalent bonding between the anchored polymer molecule and the substrate surface [7–11]. Therefore, the solid material used as a substrate should have reactive groups in an area accessible to the polymer reactive groups [12,13]. Polyethylene (PE) is an attractive surface modification material due to its good bulk properties; however, PE has to be previously modified to receive the polymer layer [14–19].

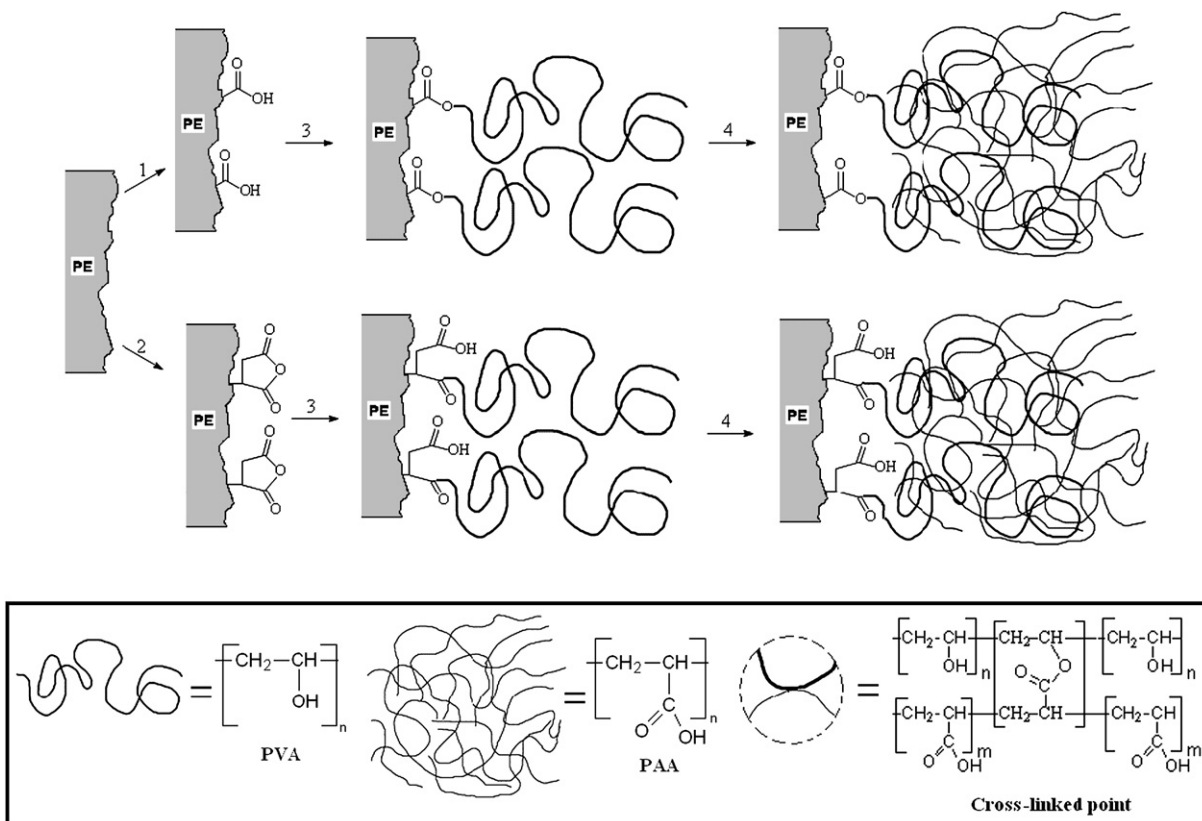
The present work aimed to develop simple and reproducible strategies to obtain multiple polymer ultra-thin layers anchored to PE films modified by surface chemical functionalization techniques. The techniques used restricted the chemical functionalization to

a thin surface layer. Carboxylic acids groups may be generated on the surface of PE films by oxidation with chromic acid, as demonstrated by Whitesides and co-workers in previous papers [20–26]. Another possibility is to generate anhydride groups on the PE film surface by radical grafting of maleic anhydride [27,28]. The small hydrophilic groups generated on the surface of the hydrophobic macromolecules are stable at room temperature [24]. However, the polymer surface reconstruction process may take place in few minutes when the functionalized surface is exposed to high temperature under vacuum [22]. The dilution of the hydrophilic groups in the bulk material changes the groups available at the interface.

The procedure used in this work to anchor the first polymer layer to the functionalized substrate minimizes the effect of the polymer surface reconstruction process. The attachment of the first layer happens above the substrate (PE) melting temperature and below the melting temperature of the poly(vinyl alcohol) (PVA) coat on the PE substrate. The melted functionalized substrate (PE) allows the migration and the orientation of its hydrophilic groups in relation to the interface with the hydrophilic PVA polymer. In addition, the procedure used favors obtaining high conversion values in the esterification reactions between the groups on the substrate surface and the polymer coat functional groups. This results in an anchored layer with a high density of anchored macromolecules per surface area unit.

A polymer with groups that are reactive to the groups of the first layer was used in the anchoring of the second layer. Poly(acrylic acid) (PAA) was chosen due to its carboxylic acid groups and also

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Scheme 1. Schematic representation of the chemical reactions proposed for the PE modification procedures.

because PAA can form miscible blends with PVA used in the first layer [29]. The miscibility of PVA and PAA allows anchoring in different ways, such as trains, loops, and tails, generating a firmly and irreversible linked second layer. The interpenetration of PAA into the immobilized PVA layer leads to the formation of a hyperbranched polymer material by heat-induced esterification. The crosslinking reaction of poly(vinyl alcohol) (PVA) by esterification using poly(acrylic acid) (PAA) as a crosslinking reagent was investigated to obtain highly insoluble PVA materials by different authors [30,31]. Crosslinking is widely used to increase stability of thicker organic films by the formation of hyperbranched polymer where the hydrophilic polymer material is bonded to the substrate surface in several positions [18,32,33]. The cleavage of some chemical bonds, among the hydrophobic substrate and the hydrophilic material does not cause the release of the hydrophilic material.

The anchoring of the PAA layer on the solid substrate was reported in the literature as a form of introducing a polymeric ultra-thin layer with high density of carboxylic acid groups. It may be used in different applications, such as to further react with biomolecules through covalent linkages [34–38], mainly due to the stability to relation of the effect of the polymer surface reconstruction process and the stability to relation to the treatment with basic solution (as demonstrated in the present work).

2. Experimental section

Low density polyethylene (LDPE) films with thickness between 150 and 250 μm were supplied by Poliolefinas Co. (Brazil). The films were cut into 2×1 cm pieces and washed with acetone for 24 h in a Soxhlet procedure before used as a substrate in the process described next.

2.1. Chemical oxidation with chromic acid (1)

LDPE films were submersed for 5 min in a chromic acid solution prepared with 5 g of potassium dichromate (K_2CrO_7) (Nuclear, 99%) in 20 g (~ 21 mL) of concentrated sulfuric acid (H_2SO_4) (Mallinckrodt, 98%) at 70°C . The films were removed from the solution with tweezers and rinsed three times with distilled water, immersed in nitric acid at 50°C for 10 min to remove the inorganic residues formed during the oxidation process, and extensively rinsed in distilled water.

2.2. Maleic anhydride grafting (2)

Radical grafting was carried out in 80 mL acetic anhydride (Nuclear, 95%) and 4 g maleic anhydride (Vetec, 99%) mixture. LDPE films were placed in this solution and the temperature was maintained constant at 100°C . An amount of 0.22 g of benzoyl peroxide (Riedel-de Haen, 98%) was added to the mixture as a free radical source. LDPE films stayed in the solution for 6 h. In the sequence, the films were removed from the solution, submersed in acetone for 12 h and rinsed three times with water.

2.3. PVA-anchoring procedure (3)

The functionalized films produced by either process 1 or 2 were put in Petri dishes and covered with a 5% (w/v) poly(vinyl alcohol) solution. PVA (88% hydrolyzed with M_w in the range 13,000–23,000) was obtained from Aldrich and used as received. The Petri dishes were maintained in oven for 24 h at 70°C for solvent evaporation. In the sequence, the temperature was increased to 140°C and maintained for 2 h. After the thermal treatment, the samples were submitted to Soxhlet extraction for 10 h (~ 50 cycles) using distilled water to eliminate PVA not bound to the substrate.

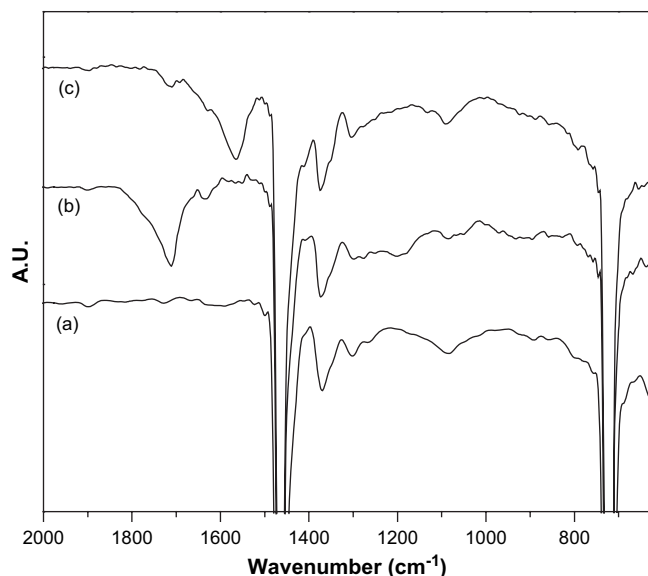


Fig. 1. ATR-FTIR spectra of (a) virgin PE, (b) oxidized PE, and (c) oxidized PE film treated with a basic solution.

performed in SHIMADZU SS-550 for morphological characterization. X-ray photoelectron spectra (XPS) were obtained with a Perkin-Elmer in Phi model 5300 ESCA system using a magnesium anode ($K_{\alpha} = 1253.6$ eV) operating at 400 W. The binding energies cited here are referenced to the saturated carbon photopeak (C1s) at 285.0 eV.

3. Result and discussion

3.1. PE functionalization

The functionalization of the PE film surface was accomplished by two methods. In the first one, the PE surface was chemically oxidized with chromic acid [20–26]. Chromic acid is generated in acidic solution of either chromate or dichromate salt. It is a powerful oxidant, being capable of oxidizing hydrocarbons with the resulting formation of alcohols, aldehydes, ketones, and carboxylic acids. However, selective formation of carboxylic acid occurs in the oxidation of PE film with chromic acid. In the ATR-FTIR spectrum of oxidized PE, Fig. 1, it can be verified a signal at 1713 cm^{-1} attributed to a carbonyl stretching absorption band not present in the virgin PE film spectrum. This signal shifts almost totally to 1565 cm^{-1} when oxidized PE is treated with a 1 M solution of NaOH at $50\text{ }^{\circ}\text{C}$ for 2 h. The signal at 1565 cm^{-1} is due to the carbonyl stretching absorption band of carboxylate. The remaining small signal at 1713 cm^{-1} may be attributed to the presence of aldehyde and ketone groups. The presence of alcohol groups cannot be verified by the absence of hydroxyl vibrational modes.

The second functionalization method used was radical grafting of maleic anhydride to PE. Maleic anhydride attaches to PE in the form of succinic anhydride, as shown in Scheme 1 [27,28]. The anhydride-functionalized surface was characterized (Fig. 2) by the presence of anhydride peaks in the ATR-FTIR spectrum at 1785 and 1720 cm^{-1} due to the asymmetric and symmetric carbonyl stretching modes. The signals at 1184 and 918 cm^{-1} appear in the spectrum as a result of C–C(=O)–C(=O)–C stretching vibrational modes of cyclic anhydrides. The reactivity of anhydride groups was tested treating the sample with a 1 M solution of NaOH at $50\text{ }^{\circ}\text{C}$ for 2 h. The treatment of the maleic anhydride-functionalized film with a basic solution promoted the incomplete hydrolysis of the anhydride groups and the partial neutralization of the carboxylic acid formed in the hydrolysis. This can be visualized in the ATR-FTIR

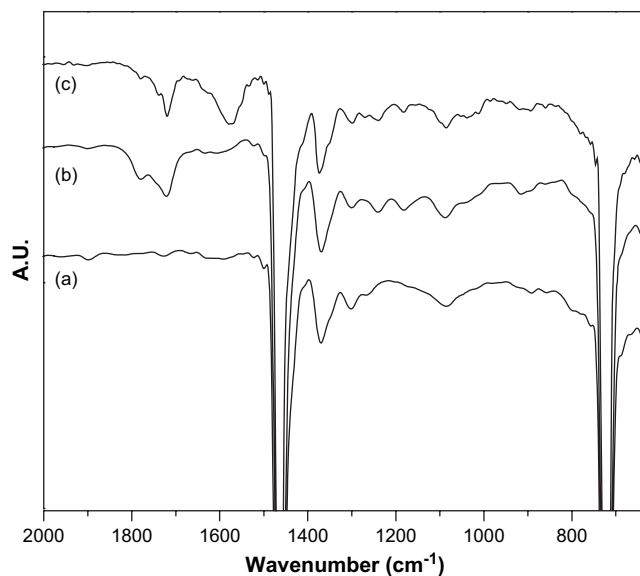


Fig. 2. ATR-FTIR spectra of (a) virgin PE, (b) PE grafted with maleic anhydride and (c) PE grafted with maleic anhydride and treated with a basic solution.

spectrum (Fig. 2) of the film after the treatment with the basic solution. We can also see a decrease in intensity of the bands at 1785, 1184, and 918 cm^{-1} attributed to the anhydride peaks. The signal at 1720 cm^{-1} due to the C=O stretching of carboxylic acid from the anhydride hydrolysis overlapped with the symmetric carbonyl stretched mode signal of the remaining anhydride groups. At 1576 cm^{-1} , it appeared a more intense signal due to the C=O stretching of carboxylate from the neutralization of the carboxylic acid formed in the hydrolysis. The reaction of the anhydride groups with a concentrated NaOH solution is a quantitative one. The incomplete conversion of the anhydride with the basic solution is associated with the presence of anhydride groups in regions inaccessible to the basic solution. The functionalization of the PE films by heterogeneous reaction generates a three-dimensional spatial distribution of functional groups in the surface region [21]. The concentration of the functional groups is maximum on the upper surface and decreases from the surface to the bulk, where the concentration approaches zero. The penetration of the aqueous solution in contact with PE, a very hydrophobic polymer, in the polymer film is limited to the upper surface region and depends on the concentration of the functional groups. Consequently, functional groups buried in a surface region with a low concentration of functional groups, a hydrophobic region, are inaccessible to the aqueous solution. The groups inaccessible to the aqueous solution are sensitive to ATR-FTIR. The infrared radiation penetrates approximately one-quarter of the observation light wavelength (1200 nm at 1700 cm^{-1}) [20].

The surface morphology of the oxidized film is different from that of virgin PE. By comparing SEM images of oxidized and virgin PE films, Fig. 3a and b, respectively, one notices a clear change on the film surface with the emergence of several holes distributed all over the surface of the oxidized film. The AFM images of the virgin (Fig. 4a) and oxidized PE films (Fig. 4b) show that the oxidation process promotes an increase in film surface roughness. The RMS of the virgin PE is 19.7 nm and the RMS of the oxidized PE is 25.0 nm. A SEM micrograph of the maleic anhydride-grafted film is given in Fig. 3c. The surface presents regular arrays all over the film surface, differently from the virgin PE film surface. The structures formed on the surface of the maleic anhydride-grafted film are best visualized by AFM. The AFM image of this sample, Fig. 4c, shows well defined hill-like structures uniformly distributed on the film surface. The RMS of the maleic anhydride-grafted film is 58.5 nm. The surfacing

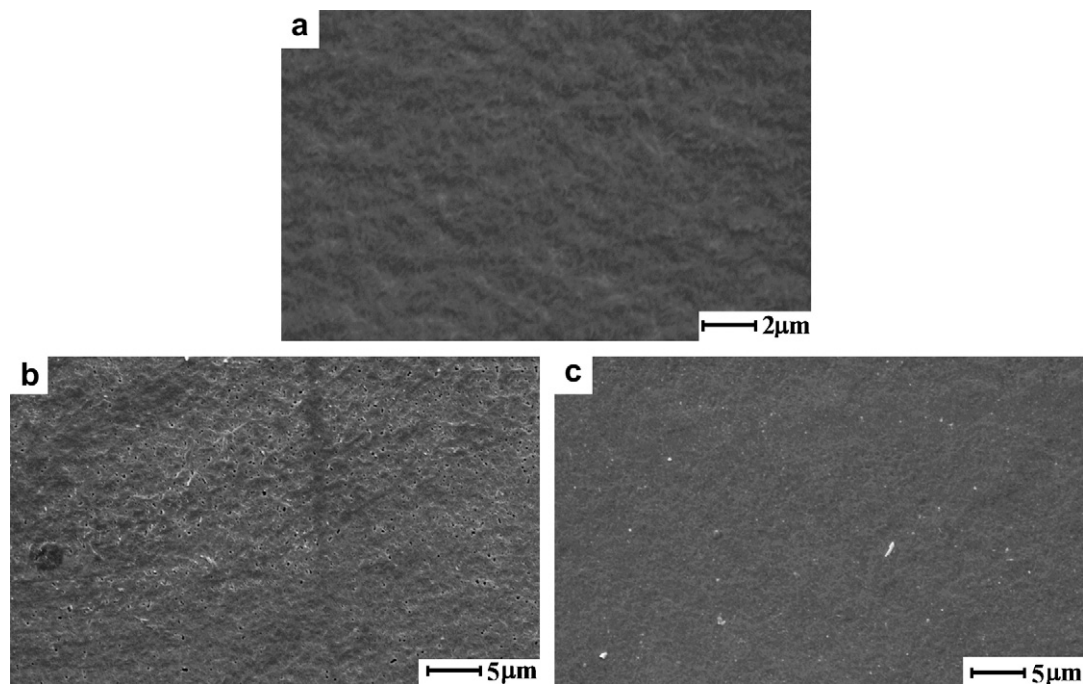


Fig. 3. SEM micrograph of (a) virgin PE, (b) oxidized PE, and (c) PE grafted with maleic anhydride.

of these structures results from the PE film surface deformation. The modification process increases the compatibility of the substrate surface with the solution, causing a decrease in the interface tension. The deformation process results in an increase in the interface area, which is facilitated by the long reaction time and the reaction temperature, near the substrate melting temperature. The hill-like surface structures formed in the maleic anhydride grafting were maintained because the films were removed from the solution at 100 °C and immediately immersed in acetone at room temperature.

3.2. Anchoring of the first polymer layer

The PVA grafting was started by the formation of a PVA layer on the functionalized PE films by evaporating the solvent from a PVA solution. The deposition of PVA onto the functionalized PE made the physical contact among the PVA hydroxyls and functional groups, either carboxylic acid or anhydride, present on the surface of the functionalized PE possible.

PVA and PE are both semi-crystalline polymers. The anchoring reaction is performed at a temperature above the PE melting point (~ 113 °C) and below the PVA melting point (~ 222 °C). The rigid form of the PVA film around PE melted during the thermal treatment allows keeping the physical form of the substrate. The mobility of the PE macromolecules permits the migration and the orientation of the hydrophilic groups (carboxylic acid and anhydrides) towards the interface, reducing the interface tension between the hydrophilic PVA and the hydrophobic PE.

After the thermal treatment, the substrates coated with the PVA layer were submitted to an intense Soxhlet extraction process aiming to remove the PVA molecules not covalently linked to the substrate surface. The ATR-FTIR spectra of PVA grafted to carboxylic acid- and anhydride-functionalized PE film surfaces are shown in Figs. 5c and 6c. The achievement of PVA grafting is confirmed by the presence of characteristic PVA bands at 3360 cm^{-1} due to the hydroxyl stretching, and at 1091 cm^{-1} due to the C–O stretching of secondary alcohol [39]. Another PVA grafting indication is the change in the region of 1700 cm^{-1} . The broad band of oxidized PE

film (Fig. 5b) becomes narrower and centered at 1717 cm^{-1} (Fig. 5c). The double signal of the carbonyl stretching of anhydride (Fig. 6b) becomes a single signal also centered at 1717 cm^{-1} (Fig. 6c). It agrees with the conversion of carboxylic acid and anhydride to ester groups with high value. The complete disappearance of the anhydride group signals indicates that even the groups initially in deep areas, as previously pointed out, were consumed in the interface reaction.

The chemical compositions of the two PVA-grafted samples analyzed by ATR-FTIR spectra are similar, but the surface morphologies are extremely different. In the SEM micrographs in Fig. 7a and b, it is seen that the PVA-grafted sample obtained from the PE functionalized with carboxylic acid is smooth, without any surface features, whereas the surface of the PVA-grafted sample obtained from PE functionalized with anhydride is more irregular and shows some features such as varying-sized semi-spheres. The analysis of the surface topography of the PVA-grafted samples in the AFM images in Fig. 8a and b shows that it depends on the functionalized PE topography. The comparison of the AFM images of the PVA-grafted samples with the AFM images of the carboxylic acid- and anhydride-functionalized surfaces reveals that PVA anchoring smoothes out the film surface, in both cases the observed RMS is lower, the RMS values are 23.3 and 37.4 nm for the PVA-grafted samples prepared from the carboxylic acid- and anhydride-functionalized surfaces, respectively; however, the surface pattern is maintained. This finding corroborates that the deposition of a PVA layer on the functionalized substrate allows the physical contact between groups for ester formation and also acts in the maintenance of the substrate physical form.

3.3. Second polymer layer anchoring

The second layer grafting was carried out by a method similar to that used for the first layer. The methodology used favors the interpenetration of PAA segments in the PVA-grafted layer. When interfaces between two polymers are present [7], interpenetration phenomena must always be taken into account. The extension of the interpenetration depends on thermodynamic and geometric

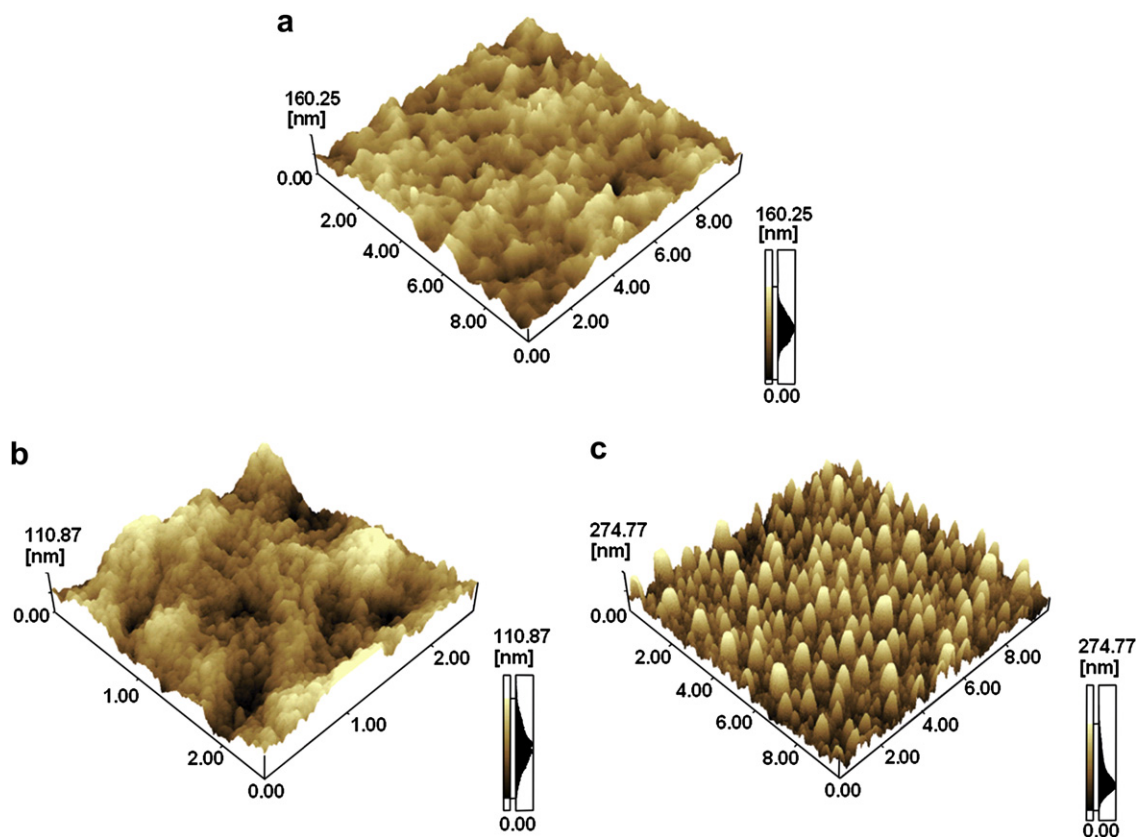


Fig. 4. AFM images of (a) virgin PE, (b) oxidized PE, and (c) PE grafted with maleic anhydride.

factors. The deposition of PAA onto the PVA layer was achieved by casting a PAA solution on the substrate at 70 °C. The large mobility of the PAA segments in aqueous solution allows their easy penetration into the PVA layer. The two polymers, PVA and PAA, are completely miscible and this fact avoids phase segregation in the interpenetration zone during the casting process. In this system, all grafted PVA groups are available for the solid state esterification with the deposited PAA.

The ATR-FTIR spectra of the substrates after the extraction of the molecules not covalently linked (Figs. 5d and 6d) reveal the success of the PAA grafting. In both samples, there appear characteristic PAA signals at 3448, 1715, and 1255 cm^{-1} relative to O–H stretching, C=O stretching, and C–O stretching modes, respectively. The PAA signals are much more intense than the PVA signals of the first grafted layer, indicating that the amount of grafted PAA is larger than that of PVA and also that the second layer is denser than the

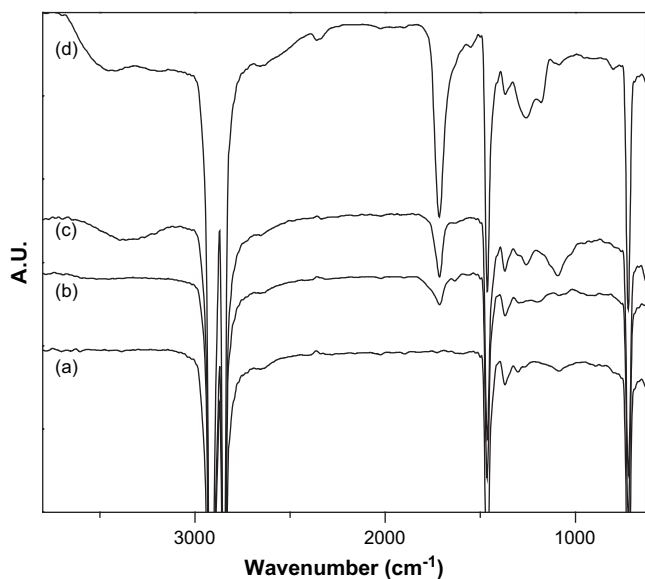


Fig. 5. ATR-FTIR spectra of (a) virgin PE, (b) oxidized PE, (c) PVA-anchored film and (d) PAA-anchored film.

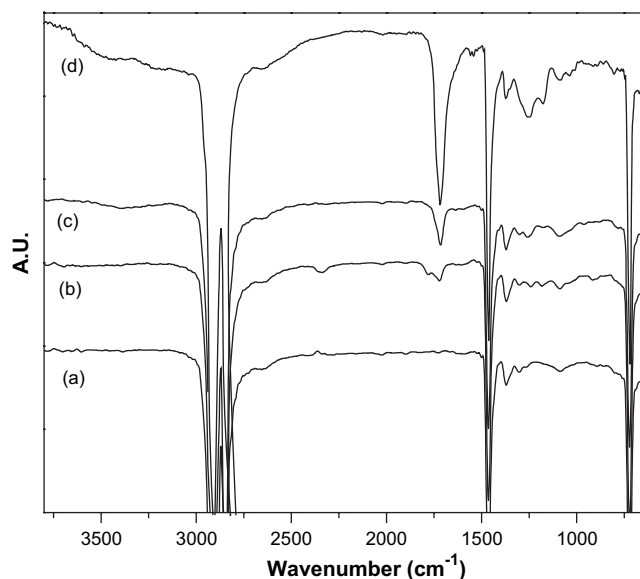


Fig. 6. ATR-FTIR spectra of the (a) virgin PE, (b) PE grafted with maleic anhydride, (c) PVA-anchored film, and (d) PAA-anchored film.

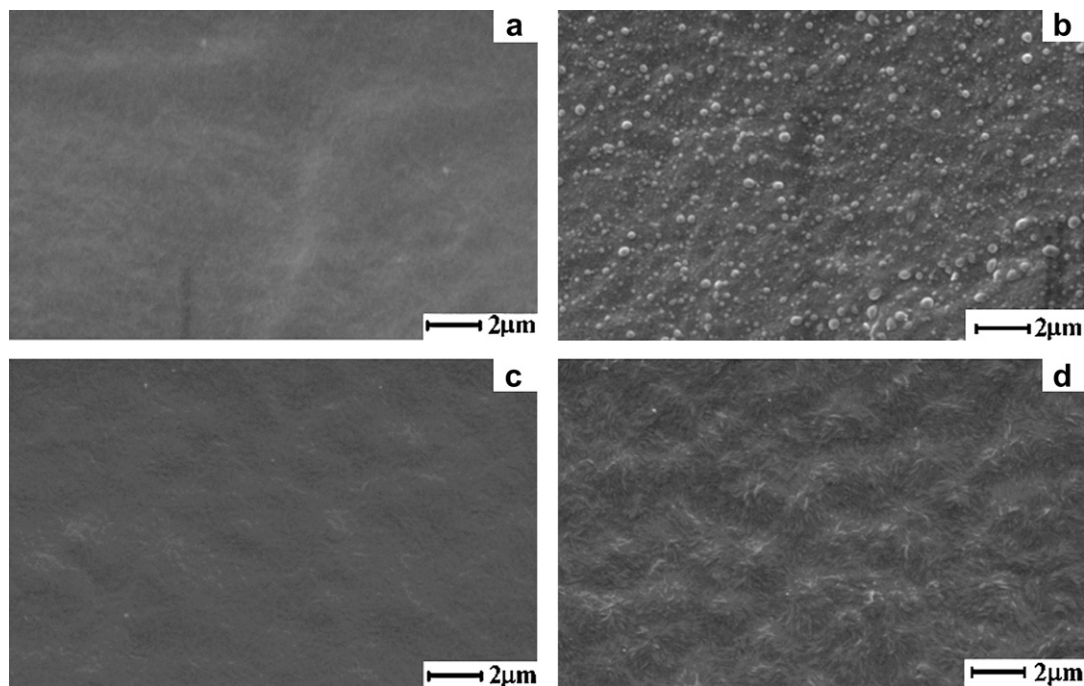


Fig. 7. SEM micrograph of the (a) PVA anchored to oxidized PE film, (b) PVA anchored to anhydride-grafted PE, (c) PAA anchored to oxidized PE film, and (d) PAA anchored to anhydride-grafted PE.

first layer. The larger amount of polymer anchored to the second layer compared to that of the first one is due to its larger quantity of reaction sites. In the first polymer layer grafting, the anchoring sites, carboxylic acid and anhydride groups, are present only in a thin surface layer generated by the functionalization processes,

while in the second polymer layer grafting, the anchoring sites, hydroxyl groups, are present in each repeat unit of the first anchored polymer layer.

Heat-induced esterification among carboxylic acid groups from PAA and hydroxyl groups from PVA promotes the stable

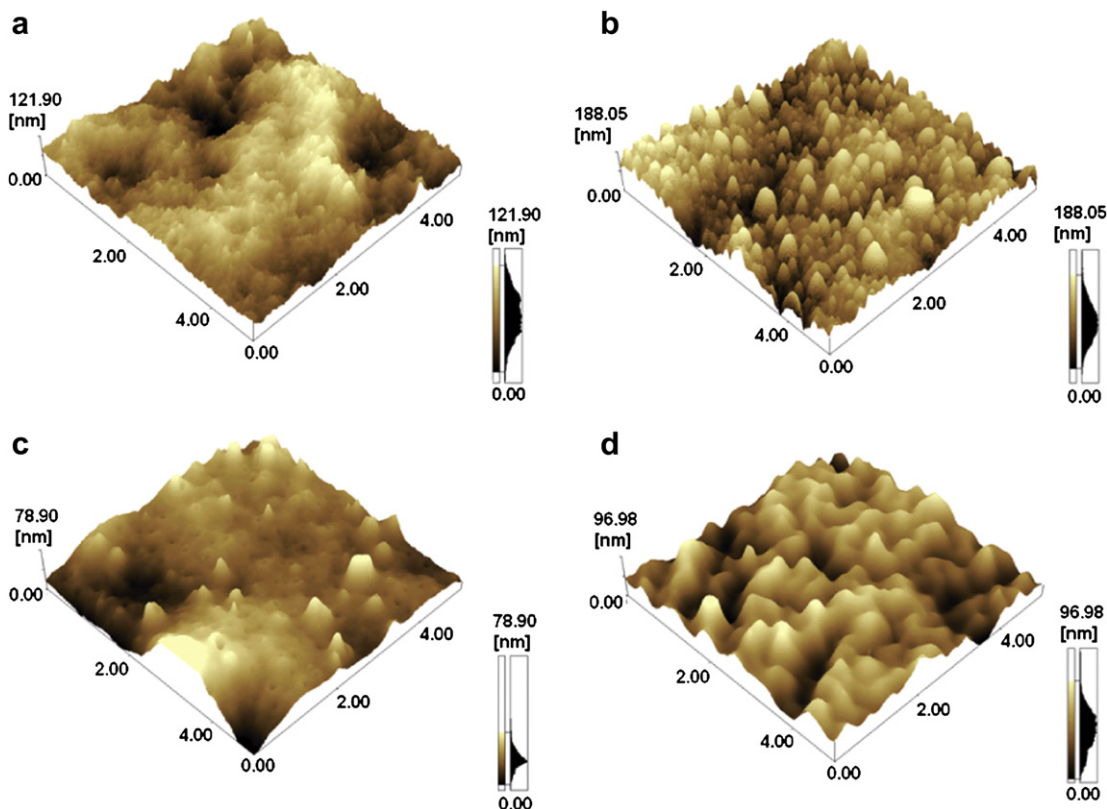


Fig. 8. AFM images of (a) PVA anchored to oxidized PE film, (b) PVA anchored to anhydride-grafted PE, (c) PAA anchored to oxidized PE film, and (d) PAA anchored to anhydride-grafted PE.

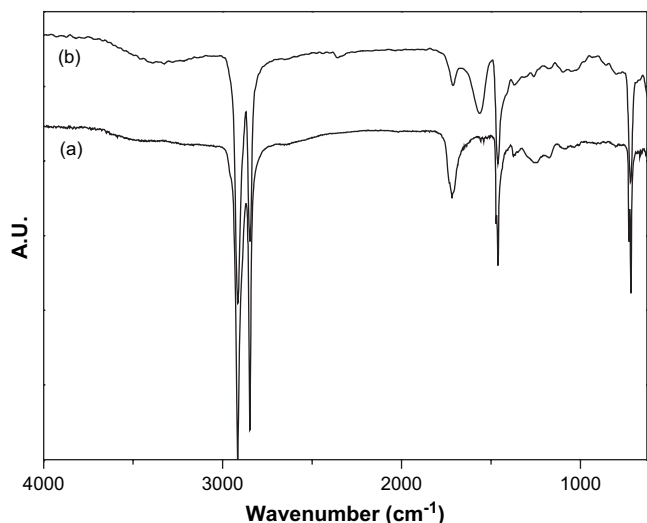


Fig. 9. ATR-FTIR spectra of the (a) PVA-anchored on PE grafted film with maleic anhydride and (b) treated with a basic solution.

immobilization of PAA chains. The stability of the modified surface and the formation of the ester groups were tested treating the modified film with a basic solution, NaOH 1 M, at 50 °C for 30 min. The ATR-FTIR spectrum of the film treated with basic solution is shown in Fig. 9. In this spectrum can be noted the splitting of the carbonyl signal, initially located at around 1720 cm⁻¹, in two distinct bands. One is located in 1562 cm⁻¹ and this band is attributed to carbonyls from carboxylate groups formed by the

neutralization of the carboxylic acid groups by the basic solution. The other band, located at 1720 cm⁻¹, is attributed to the carbonyls from ester groups. The area of the band attributed to carbonyls from ester groups corresponds to almost 30% from the area of the total carbonyl groups. This fact indicates that the PAA chains are immobilized in the surface of the film by covalent linkage and each PAA chain is bonded at several positions due to the high quantity of ester groups formed.

The surfaces of the PAA anchored to oxidized PE film and PAA anchored to anhydride-grafted PE film are flat and have different arrangements, which can be observed in the SEM micrographs shown in Fig. 7c and d and also in the AFM images in Fig. 8c and d. In both cases, the surface topography of the PAA-grafted films is smoother than those of the PVA-grafted films, the calculated RMS values are 16.1 and 18.9 nm for the PAA-grafted films obtained from carboxylic acid- and anhydride-functionalized surfaces, respectively. However, the topography of the PAA-grafted films present surface patterns similar to those of the PVA-grafted films. This fact is in agreement with our conclusion on the influence of the substrate topography on the smoothing out of the film topography after the anchoring process used in this work.

3.4. XPS studies

The chemical state of the elemental components of the surface modified polyethylene was examined by XPS. The spectra were curves resolved to yield sets of photo peaks consistent with the types and relative concentrations of the elements present. The results are presented in Figs. 10 and 11. The carbon 1s and oxygen 1s spectra were curves resolved into different peaks considering the

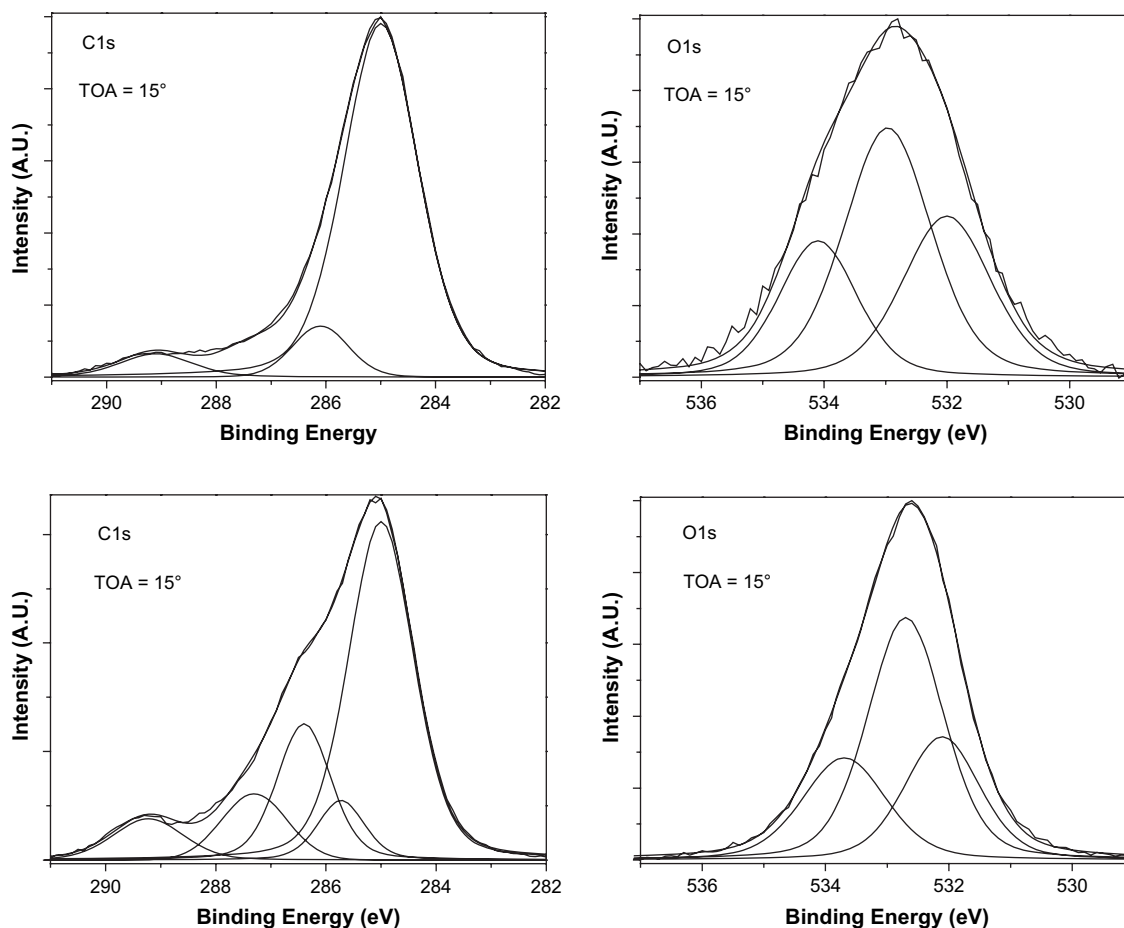


Fig. 10. Carbon 1s and Oxygen 1s XPS spectra of PE grafted with maleic anhydride (top) and PVA-anchored film (bottom).

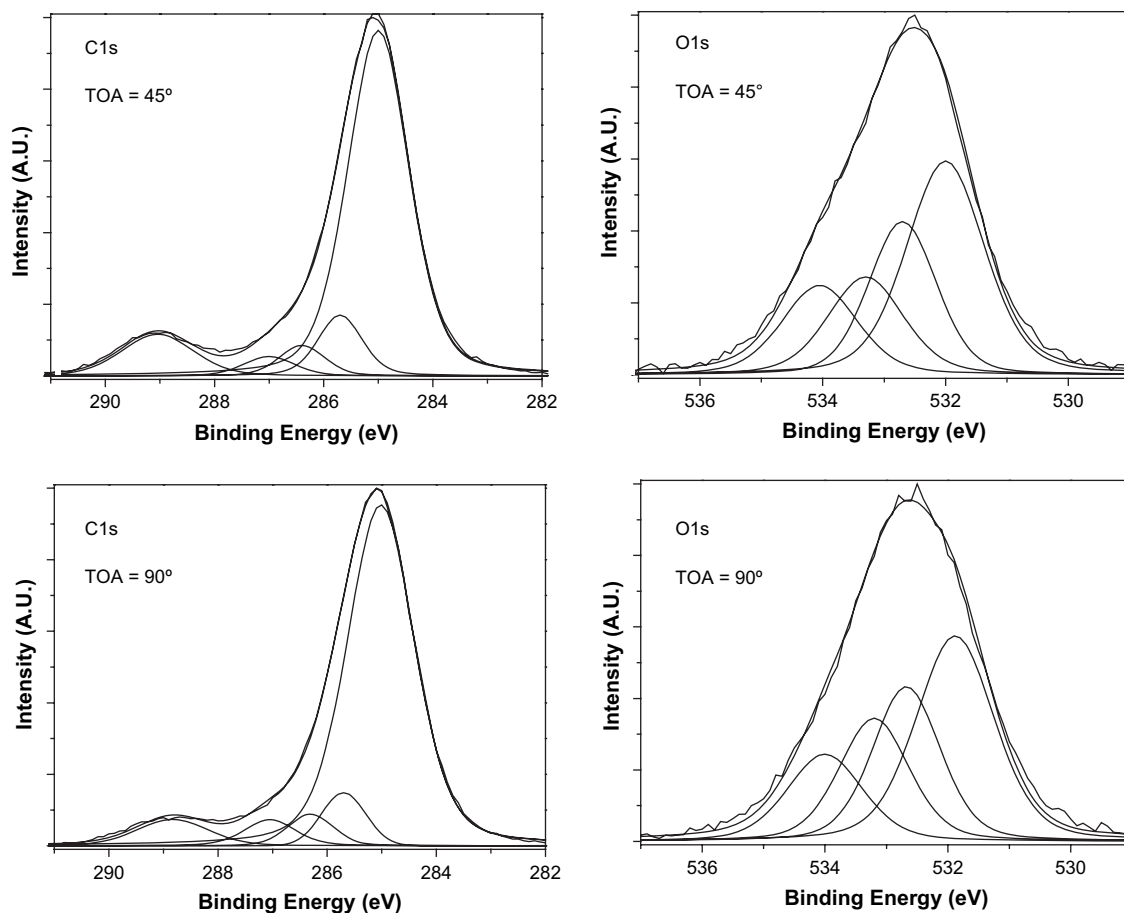


Fig. 11. Carbon 1s and Oxygen 1s XPS spectra of PAA-anchored film at take-off angle = 45° (top) and take-off angle 90° (bottom).

expected groups in each modified PE surface. The data obtained in the deconvolution are organized in two tables. In Table 1 are presented the data from the carbon 1s spectra and in Table 2 are presented the data from the oxygen 1s spectra.

The XPS data are in agreement to the ATR-FTIR data. The XPS spectrum of maleic anhydride-grafted film (PE-g-MA), in low takeoff angle (15°), demonstrated the presence of carbon and oxygen with elemental atomic concentration of 86.9% and 13.1%, respectively. In the spectra of the maleic anhydride-grafted film (PE-g-MA) is verified the presence of peaks whose positions are characteristics of anhydride groups (Tables 1 and 2). The immobilization of PVA on the surface of the maleic anhydride-grafted film (PE-g-MA/PVA) is confirmed by the increase of oxygen atomic concentration from 13.1% to 27.7% in the same takeoff angle (15°), and also by the presence of the peak at 286.3 eV attributed to carbon directly bonded to hydroxyl groups of PVA (C–OH). In this sample is noted the increase of the C=O carbons in almost 20%, PVA used in this procedure is 88% hydrolyzed, consequently, 12% of

the repetitive units of PVA have carbonyl groups. The formation of the ester groups is evidenced by the carbon peak at 287.1 eV (C–O–C=O) and by the oxygen peak at 534.0 eV (C–O–C=O).

The PAA-grafted film (PE-g-MA/PVA/PAA) was analyzed by XPS in two takeoff angles (TOAs) (45 and 90°) in order to study the in-depth distribution of the chemical composition (Fig. 11). The sampling depth of XPS is related to the relative orientation of the incident X-ray beam and the sample surface. The value of the sampling depth, l , for each takeoff angle can be calculated according to Eq. (1):

$$l = 3\lambda \sin \theta \quad (1)$$

where λ is the inelastic mean free path of the electrons (ca. 40 Å for the C 1s from PE) and θ is the takeoff angle [40].

In both spectra are demonstrated the presence of the PAA components. The relative area of components in the oxygen 1s XPS spectra is very similar in both takeoff angles, indicating a uniform

Table 1

Relative area fraction of components in C 1s XPS lines found by curve fitting; the photoelectron take-off angle (TOA) is also specified

Carbon 1s [41]	PE-g-MA/PVA		PE-g-MA/PVA/PAA	
	TOA = 15°	TOA = 15°	TOA = 45°	TOA = 90°
C–C (285.0)	0.818	0.566	0.729	0.775
C–C=O (285.7)	0.085 ^a	0.073	0.093	0.071
C–OH (286.3)	–	0.189	0.047	0.047
C–O–C=O (287.1)	0.045	0.101	0.033	0.045
C=O (289.0)	0.052	0.071	0.098	0.062

^a Carbon signal from anhydride shifted to 286.1 eV (C–(C=O)–O–C=O).

Table 2

Relative area fraction of components in O 1s XPS lines found by curve fitting; the photoelectron takeoff angle (TOA) is also specified

Oxygen 1s [41]	Surface			
	PE-g-MA/PVA		PEgMA/PVA/PAA	
	TOA = 15°	TOA = 15°	TOA = 45°	TOA = 90°
C=O (532.0)	0.466	0.257	0.408	0.385
C–OH (532.7)	–	0.507	0.248	0.251
HO–C=O (533.3)	0.305 ^a	–	0.180	0.207
C–O–C=O (534.0)	0.229	0.236	0.164	0.157

^a Oxygen signal from anhydride shifted to 533.0 eV (O=C–O–C=O).

distribution of the oxygen functions in the modified layer, however, the atomic concentrations of the oxygen decrease from 21.4%–16.1% when the takeoff angle is increased from 45 to 90°, comparing measurements with sampling depth of ~8.5 and ~12 nm, calculated by Eq. (1). The relative area of the C=O peak (289.0 eV) compared to C–C peak (285.0 eV) decreased by 40% when the sampling depth is increased to ~8.5 and ~12 nm. These findings unequivocally demonstrate the formation of PAA-rich region (PAA layer) on the surface of PE-g-MA/PVA. The thickness of the modified surface layer is approximately few dozens of nanometers (ultra-thin), for the reason that the small variation in the depth of analysis, caused by the variation in the takeoff angle, is able to detect a change in the relative amount of PE-g-MA/PVA and PAA.

4. Conclusion

Chemical oxidation with chromic acid and radical grafting of maleic anhydride to the surface of PE film are suitable methods for introducing immobilized reactive groups to the surface of PE. In the oxidation with chromic acid, all carboxylic acid groups formed are accessible to react with a basic aqueous solution; hence all carboxylic acid groups are immobilized in a very thin surface layer. In contrast, in the maleic anhydride radical grafting of the PE film, a fraction of the anhydride groups is inaccessible to the basic aqueous solution; consequently, these groups are some nanometers above the surface, in a region sensitive to ATR-FTIR, but inaccessible to the basic aqueous solution.

The procedure used in this work promoted the anchoring of PVA to the functionalized film and produced an ultra-thin layer covalently linked by esterification, which occurred with a high degree of conversion. Reactive groups, such as anhydride groups inaccessible to the basic aqueous solution and groups that migrate to the bulk due to the surface reconstruction process, were consumed in the esterification.

The PVA-anchored layer and PAA of the second anchored layer are firmly bound to the PE substrate. In the anchoring process of the second polymer layer, a larger amount of polymer is anchored when compared to the amount of the first anchored polymer layer.

The substrate surface topography in the nanometer scale is partially maintained after the polymer anchoring, being only smoothed out, which depends on the amount of anchored polymer and the substrate roughness.

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