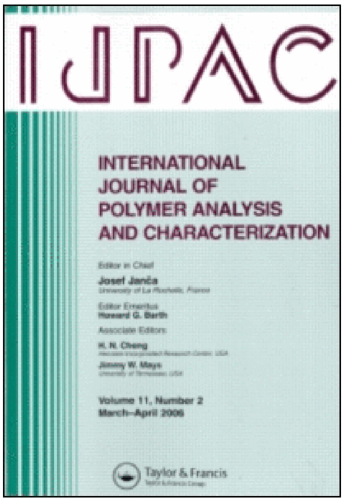

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CHARACTERIZATION OF STRUCTURAL MODIFICATIONS INDUCED ON POLY(VINYL ALCOHOL) SURFACE BY ATMOSPHERIC PRESSURE PLASMA

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The surface properties of polymers are of great interest to researchers. With significant growth in global demand due to its properties and availability to be processed, poly(vinyl alcohol) is at the top of common polymers. This article is concerned with plasma treatment applied on poly(vinyl alcohol) surfaces and their characterization by various methods. After plasma treatment, the roughness of the polymeric films is changed; topographical modifications of the samples were also observed. Moreover, the new fine features of PVA surface, formed due to the DBD plasma treatment, have different dimensions, depending on the plasma treatment duration.

***Keywords*:** Atomic force microscopy; Plasma treatment; Poly(vinyl alcohol) film; Swelling; X-ray photoelectron spectroscopy

INTRODUCTION

Among polymers with ecofriendly properties stands out poly(vinyl alcohol) (PVA) with a wide variety of applications and increasing market demand. It is recognized as one of very few vinyl polymers soluble in water. Its biodegradability, biocompatibility, and nontoxicity,[1,2] combined with its semicrystalline character and its ability to form hydrogen bonding, makes it an ideal choice as adhesive, textile wrap sizing, polarizer,[3] membrane with selective permeability, medium for controlled drug delivery,[4–6] wound dressing, and artificial skin.[2] Due to its properties, PVA is also preferred as a matrix for (nano)composite materials. All these applications are in contrast to its very simple structure containing a carbon backbone with hydroxyl groups attached. The basic properties of PVA depend on the degree of polymerization, degree of hydrolysis, and tacticity of macromolecular chains.

A growing interest of researchers is to modify the polymer surface in order to tailor optimal material for a certain application for industry, medicine, or biology. Using different work conditions and investigation techniques it is possible to provide and determine the changes of the polymer surface properties.

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The treatment of materials by nonthermal plasma is an alternative most used when it is necessary to change and/or to improve some surface properties, such as morphology, hardness, wettability, resistance to scratching, adhesion, and biocompatibility. For surface modifications, the atmospheric plasma treatment is preferred because it does not affect bulk properties of materials and it is environmentally friendly.[7] Due to its simplicity and homogeneous character,[8] atmospheric pressure dielectric barrier discharge (DBD) is obviously attractive for applications in comparison to high-cost vacuum-based plasma processes. The plasma treatments that use DBD in air or in other gases or vapors, such as helium, argon, oxygen, or mixtures thereof, and that run at or near atmospheric pressure are very convenient for the activation or modification of polymer surfaces.[9] After plasma treatment, the polymer surfaces can be functionalized with different chemical compounds that can be attached by physical or chemical bonds. The literature reports related to plasma treatment of PVA refer to its desizing from cotton and rayon fabrics.[10,11] However, information about plasma surface treatment of this polymer is poor.[12–14]

In this context we focused our research on the investigation of some characteristics of PVA films after atmospheric DBD plasma treatment. The modifications in the properties of PVA that are observed are presented in comparison with those of untreated polymer. PVA film properties have been assessed through the combined use of atomic force microscopy (AFM), attenuated total reflectance Fourier transform-infrared (ATR FT-IR) spectroscopy, and X-ray photoelectron spectroscopy (XPS) measurements. The swelling behavior of PVA films was also investigated.

EXPERIMENTAL SECTION

Materials and Samples Preparation

Industrial grade PVA, supplied from the Chemical Plant Rasnov, with average molar mass $M_w = 39600\,g/mol$ has been used without further purification. The polymer is amorphous and atactic with a degree of hydrolysis of 92%.

The polymer was studied in the solid state, as thin films. The starting solution (7% w/v) of polymer was prepared by dissolving PVA powder in pure water and heating gently to 70–80°C in a water bath to prevent thermal decomposition of the polymer. The hot solution was continuously and slowly stirred (about 4–5 h) until the polymer completely dissolved and formed a clear viscous solution. Then, the solution was left to cool at room temperature, and subsequently it was filtered and degassed in an ultrasonic bath. The films obtained by the casting method on a flat glass plate were left to dry in air for three days, and they were further dried in a desiccator at room temperature. The samples for swelling and solubility testing were cut from the PVA films into strips 1.0 cm × 5.0 cm in size.

Plasma Treatment of PVA Films

The polymer films were treated in asymmetrical DBD plasma, with two copper electrodes, glass as a dielectric, and an applied voltage of 9 kV with a repetition rate of 2 kHz. The working gas was helium of spectral purity 99.99% (controlled flow rate, $Q_{He} = 3\,L/min$) at atmospheric pressure. The plasma treatment procedure was detailed elsewhere.[15] The polymer samples were placed on the ground electrode and treated on both sides for 10 and 20 s.

Sample Characterization

The investigation of polymer films was performed by different versatile methods related to surface properties (ATR FT-IR, AFM, XPS) and bulk properties (swelling and solubility). The results of analyses were correlated for better characterization of PVA films before and after plasma treatments.

The ATR FT-IR spectra of the polymer films were recorded at 25°C, over the range 4000–400 cm^{-1} using a Bruker Vertex 70 spectrometer. The internal reflection element was a single reflection diamond ATR crystal with an incidence angle of 45°. One hundred scans at a resolution of 2 cm^{-1} were averaged to obtain each spectrum.

The AFM technique was used to characterize changes in the surface morphology of PVA films induced by plasma treatment. AFM measurements were performed on a Solver PRO-M microscope (NT-MDT, Russia) operating in the tapping mode at room temperature with 0.1 nm resolution in z direction. The standard silicone nitride cantilever (NSC21) and tip radii less than 10 nm were used. The AFM technique permits characterizing surface roughness by means of different texture parameters, such as average roughness (R_a) and root-mean-square roughness (R_{rms}), dimension of topological peaks, and their distribution on the surfaces.[16]

XPS used to study the changes of the polymer film surface caused by the plasma treatment was performed on a PHI 5000 Versa Probe X-ray photoelectron spectrometer equipped with a conventional hemispherical analyzer. The X-ray employed was a monochromatized Al K_α (1486.7 eV) source operating at 24.2 W. The analysis area was 0.1 mm^2 (100 μm × 100 μm) using a takeoff angle of 45° relative to the surface normal. The measurements were carried out in a vacuum atmosphere (around 10^{-7} Pa). The binding energy scale was corrected for static charging, using an electron binding energy of 285.0 eV for the C1s level of aliphatic hydrocarbons.

PVA belongs to the class of polymers that have sufficient nonpolar interchain interactions to show saturation swelling behavior, i.e., it does not dissolve completely even on prolonged exposure to water.[17] For swelling and solubility testing, the films were immersed in water under identical conditions. Each piece was weighed (W_1) and immersed in a test tube containing distilled water. The test tube was then placed in a bath that was kept at desired and controlled temperature for a chosen time. The films were removed, wiped dry to remove water, and weighed (W_2). Then, the films were dried in an oven at 40°C until a constant weight was achieved (W_3). For each piece, the percent weight change and percent swelling were calculated. The weight change (solubility) of the PVA films was calculated as follows:

$$\%\ \text{weight change} = \frac{(W_1 - W_3)}{W_1} \times 100 \tag{1}$$

Swelling related to the dry state, namely percent hydration or swelling index, can be expressed as:

$$\%\,\mathrm{H} = \frac{(\mathrm{W}_2 - \mathrm{W}_3)}{\mathrm{W}_3} \times 100 \qquad (2)$$

RESULTS AND DISCUSSION

In these experiments, a simple technique was used based on a DBD that allows the production of homogeneous and high fluxes of active species and modification of the roughness of PVA film surfaces at the nanometer scale without significant surface damage.[18] The polymer film surface undergoes elimination of hydrogen and breaking of ester bonds from acetate residues, with free radical formation, repetitive chain scissions, and cross-linking under the influence of active species (ions, free radicals, and electrons) from the plasma. The created radicals at the polymer surface react with radicals present in the plasma gas to generate polar groups (hydroxyl, carbonyl, and carboxyl) that lead to increase in the hydrophilicity of the polymer. The possible reactions for free radical formation caused by plasma treatment are displayed in Figure 1.

The structural features of the polymer samples have been successfully ascertained by ATR FT-IR. Figure 2 presents ATR FT-IR spectra of PVA samples under study before and after plasma treatment.

All ATR FT-IR spectra exhibit the characteristic absorption bands typical of PVA, which can be assigned to vibrations of the C=O, C–H, C–OH, C–O bonds.[19] For plasma-treated films it can be noticed that some observable changes appear in the spectral features of the samples in the range 4000–600 cm^{-1}. The band observed at 3294 cm^{-1} associated with O–H stretching appears slightly broader, indicating the presence of both hydrogen-bonded and free hydroxyl groups. After plasma processing of PVA film, the intensity of O–H stretching band (3294 cm^{-1}) increased, due to hydrogen bond reorganization. The C–H stretching vibration region (2800–3000 cm^{-1}) is discussed below. In this region, the CH_2 symmetric (ν_s) and antisymmetric (ν_{as}) stretching vibration bands are particularly notable. The position of the antisymmetric and symmetric CH_2 stretching vibration bands at 2917 and

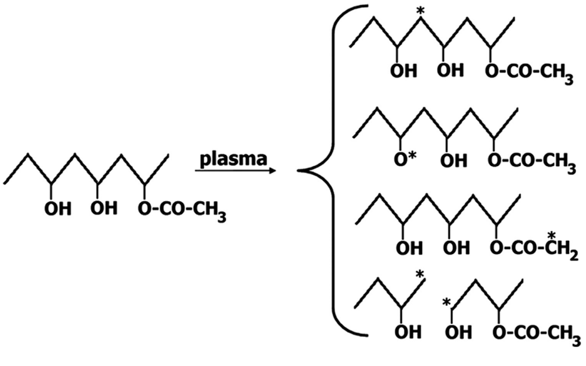


Figure 1. Possible free radical formation by plasma treatment.

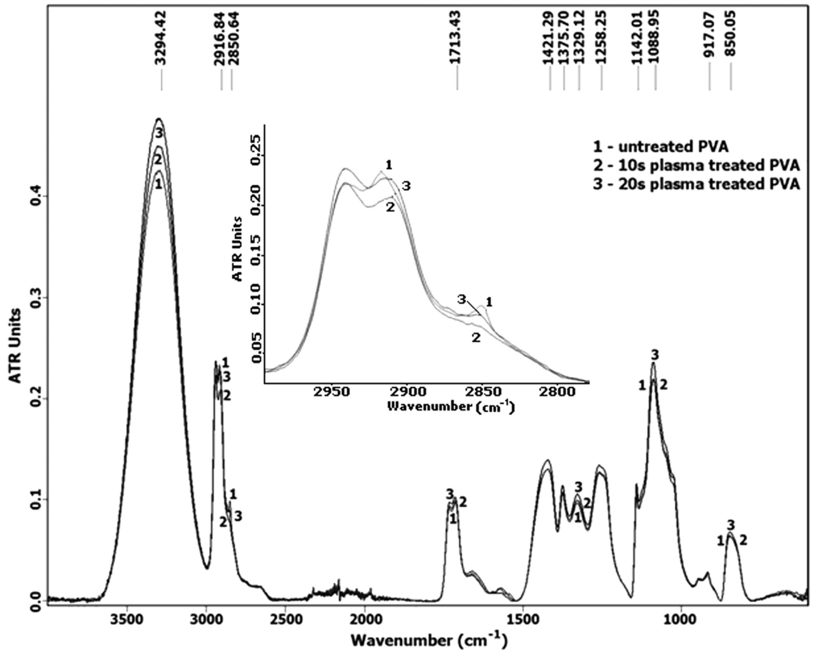


Figure 2. ATR FT-IR spectra of pure PVA and PVA plasma treated. Inlet: 3000–2800 cm^{-1} region.

2851 cm^{-1} suggests that the hydrocarbon chains of polymer take a *trans* zigzag conformation.[20] It is well known that PVA has a planar zigzag structure like polyethylene.[21] The two stretching vibrations of CH_2 groups are weaker for the sample that was treated 10 s, but they increase when the exposure to DBD plasma continues. The significant changes in the intensity of the bands at about 2875 and 2940 cm^{-1}, assigned to methyl groups, originate from acetoxyl residues observed in the case of the sample treated for more than 10 s. The residual acetate groups, resulting from manufacturing, handling, and degradation of the polymer,[22] exhibited peaks at 1713 cm^{-1} (C=O stretching), 1376 cm^{-1} (C–H bending), and 1258 cm^{-1} (C–O bending). The band at 1713 cm^{-1} increases in intensity after plasma treatment, showing incorporation of oxidized functionality on the film surface. In complement to C–H stretching vibration, the C–H deformation bands at 1421 cm^{-1} (CH_2) and 1329 cm^{-1} (C–H) increase and tend to become broad, presumably due to the appearance of cross-linking at the film surface. At 1142 cm^{-1} a peak correlated to the polymer crystallinity appears and it seems to increase after the plasma exposure. The bands at about 1375 cm^{-1} and 1090 cm^{-1}, which are due to C–O–H bending and C–O stretching coupled with O–H bending vibrations, respectively, exhibit the same behavior. The position of CH_2 bands at 917 cm^{-1} is present in the atactic form, but it almost disappears in isotactic PVA.[23,24] The peak at 850 cm^{-1} is associated with the CH_2 rocking mode of PVA.

Further characterization of untreated and plasma-treated PVA films was conducted by XPS analysis. This technique is able to characterize the changes of chemical elements of the outmost surfaces of samples, within the order of 1–10 nm,[25] much thinner than that of ATR FT-IR. To verify the chemical changes undergone on the PVA surface, XPS spectra for both the original and plasma-modified PVA films were taken, as shown in Figure 3.

The XPS spectra of PVA films contain mainly C1s and O1s peaks. The chemical composition for untreated and treated films is presented in Table I.

It is well known that the theoretical content of oxygen (originating only from –OH groups) in PVA is about 36%. Our result from the XPS spectrum of untreated PVA revealed that there still exists a difference between the outcome and the theoretical content of the oxygen element (see Table I). This indicates that not all OH groups are naked outwards on the PVA surface. According to Table I, the surface modification of PVA was confirmed. DBD plasma treatment creates additional oxidized functional groups. The data revealed the trend of the percentage of peak O1s, which increases by 1.6 times after the first plasma treatment step and further decreased by about 21.2%. It has been noted that the C1s carbon concentration first decreases by almost 22.5% and then it increases by about 16.0% when the treatment period was 20 s, compared to the sample treated for 10 s. The variations of O1s with respect to C1s can be correlated with the significant presence of chemical species at the PVA-modified surfaces. The experimental O/C ratio on the surface of PVA plasma treated for 10 s was found to increase by 0.39 compared to the untreated one. The variation of O/C ratio indicates the polar group formation along polymer chains and/or chain ends of the polymer at the surface of the film in the first phase of the exposure. When the action of plasma is prolonged, cross-linking reactions can occur. Although PVA belongs to a category of polymers that favors cross-linking,[26] in the case of plasma treatment, the degree of cross-linking is rather low[27] and the chain length reduction seems to be predominant, leading to an increase of polymer solubility.[28] Under the applied conditions, oxygen traces can be present in the

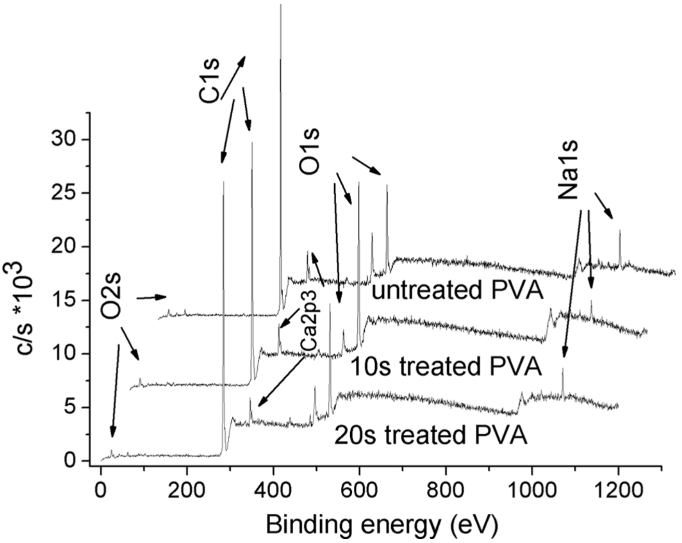


Figure 3. XPS spectra of the C1s and O1s region for the PVA samples.

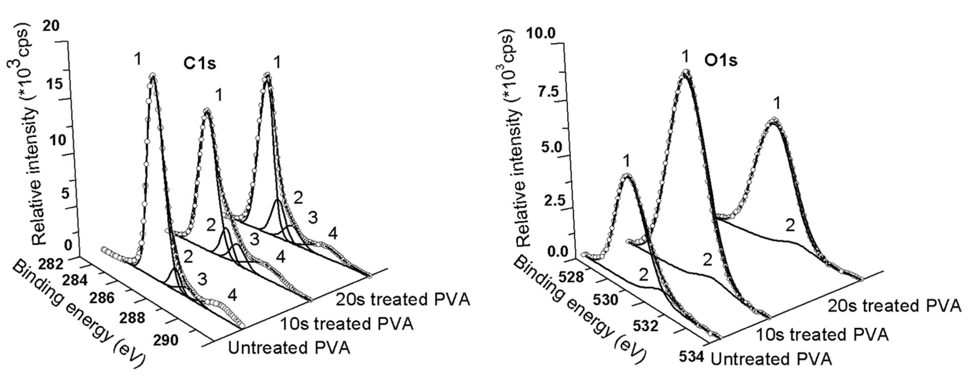
Table I. Concentration of elements in PVA samples

Sample	Chemical composition, %		
	C1s	O1s	Atomic ratio O/C
Untreated film	73.62	26.38	0.36
10 s plasma treated film	57.02	42.98	0.75
20 s plasma treated film	66.12	33.88	0.51

discharge environment. They represent a source of very reactive species that can interact with free radicals on the polymer surface, resulting in the incorporation of oxygen functional groups, as confirmed by our results. The oxygen inclusion favors the increase of the O/C ratio in the first step of the treatment and it can inhibit the cross-linking reactions.[8] In order to clarify what functional groups are on the polymer film surface and to estimate their relative amounts, a deconvolution procedure was performed on the C1s and O1s XPS spectra, as shown in Figure 4.

All peaks were labelled numerically as shown in Figure 4, and the binding energy corresponding to each peak was used to identify the chemical functional groups in the sample. Table II provides the list of functional groups with the corresponding binding energy obtained from the analysis of C1s spectra.

The XPS C1s core-level spectrum of original PVA contains a predominant peak component, C1 (C–C/C–H), and other three carbon peaks, which were associated with the methylene carbon singly bonded to oxygen C2 (C–O/C–OH), carbonyl carbon C3 (C=O), and the ester carbon atoms C4 (O–C=O/COOCH$_3$). It can be seen from C1s and O1s spectra in Figure 4 that the size of the peaks varies with the exposure time of PVA films. The bond energies associated with hydroxyl functional groups of PVA (C–OH) characteristic to this polymer can be identified at 286.1 and 531.0 eV, respectively in the C1s and O1s spectra. The final two C(1s) components at 287.6 and 288.8 eV were attributed to carboxyl and carbonyl species resulting from incomplete alcoholysis of PVA and degradation of macromolecular



(a) (b)

Figure 4. High resolution XPS spectra of (a) C1s and (b) O1s peaks for all samples. ○, original curve; solid line, fitted curve.

Table II. Surface chemical compositions for PVA samples obtained from deconvolution of XPS spectra

		Composition (%)		
Possible functional groups	Binding energy (eV)	Untreated	10 s treated	20 s treated
C–C/CH	284.8	82.21	71.58	66.95
C–O/COH	286.1	6.34	10.08	15.63
C=O	287.6	4.27	7.05	8.52
O–C=O/$COOCH_3$ and COOH	288.8	7.16	11.25	8.74

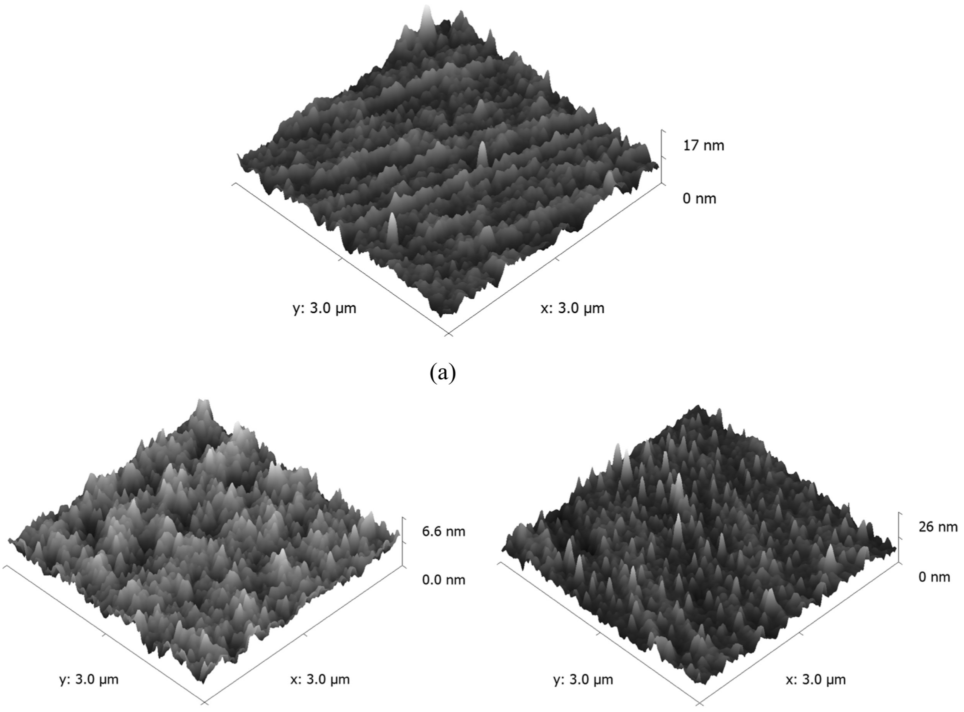
chains during the polymer synthesis. This fact is in agreement with ATR FT-IR results. It is evident that approximately 7.2% acetoxyl residues are distributed in the "near surface" region with a depth of about 5.70 nm, which is in the range of the information depth of XPS spectra obtained at a takeoff angle of 45°.[22,28] The same chemical functionalities can be identified on the treated film samples. According to Table II, oxidation is obviously demonstrated by an increase of the concentration of oxygen-containing polar groups such as C–OH, C=O, and COOR on the surface of treated PVA film and intensity of the corresponding C2–C4 peaks. This fact indicates that the radicals resulted from breaking of some C–C and C–H bonds in PVA chains, which interact with active species existing in the plasma. As can be seen in Figure 4(b), the effect of 10 s plasma treatment is reflected in the significant enhancement of the 531.0 eV component relative to the untreated polymer, followed by its decrease when exposure time is prolonged. An adverse effect of plasma exposure was observed in C1s spectra. The increase in the intensity of the C–C peak in the last step of exposure can be also attributed to the cross-linking reaction.

Chemical modifications of the polymer chains occur in parallel to physical modifications of the film surface during plasma treatment. The results obtained by XPS can be correlated with the data obtained from AFM analysis. The AFM technique is used to visualize and compare the topography of untreated and treated surfaces, as presented in Figure 5.

It can be seen in Figure 5 that plasma treatment clearly affects the topography of the polymer films. The bumps created at the PVA film surface can be explained by local modifications of the chemical structure of polymer chains. The data obtained from the analysis of the 3 μm × 3 μm AFM images are given in Table III.

Taking into account the experimental results, one can observe that the values of average roughness increase by 1.1 and 1.5 times for samples treated for 10 and 20 s, respectively, in comparison with untreated PVA film, while the root-mean-square roughness values increase by 1.35 and 1.68 times, respectively.

Swelling and solubility testing was then conducted to determine the effects of plasma exposure on polymer films. Swelling is the first stage of solvation and is directly related to material solubility. In other words, as the swelling ability of the polymer is increased, the solubility of the polymer is also increased. These properties of polymer films are important because they can be correlated with the changes in chemical structure by chain-scission and/or cross-linking due to plasma exposure. The weight change of the PVA samples related to swelling and solubility was plotted versus the immersion time in Figure 6.



(a)

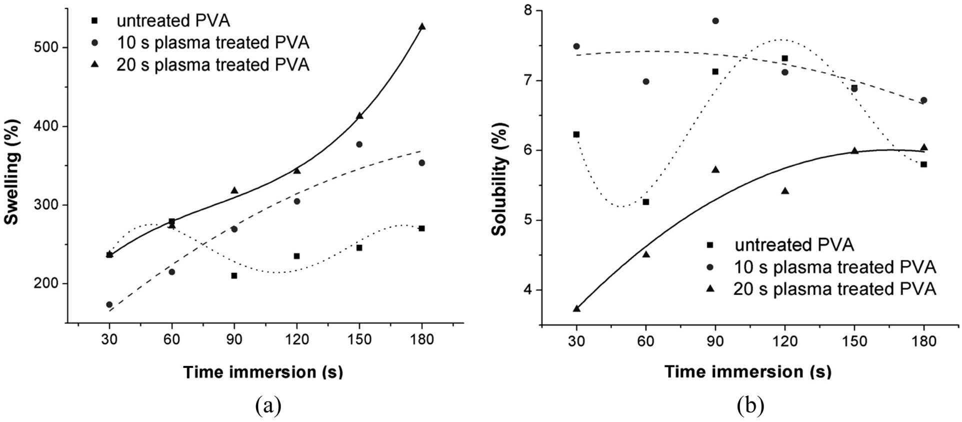
(b) (c)

Figure 5. 3-D AFM images of PVA untreated (a) and plasma-treated surfaces for (b) 10 s and (c) 20 s.

The data in Figure 6 were fitted with a polynomial function for the determination of the trend in weight changes for all samples. As shown in Figure 6(a), the swelling index of plasma-treated PVA films increases with increase of immersion time in water at room temperature. This fact can be explained by the presence of cross-linked structure induced by plasma treatment. In the case of untreated PVA, its commercial origin makes possible different behavior; thus, upon 60 s the swelling index was 279%, and then a decrease followed by an increase of swelling degree was observed. The same figure illustrates an increase in swelling index of the PVA film with increase of plasma exposure time from 10 to 20 s. As expected, the lower molecular weight chains created by chain scissions, as a result of exposure to the helium discharge, affect the degree of solubility (see Figure 6(b)). If cross-linking

Table III. Some texture parameters for all PVA samples

Sample/time exposure plasma treatment	Texture parameters	
	Average roughness R_a (nm)	Root-mean-square roughness R_{rms} (nm)
P1/0 s	1.19	1.52
P2/10 s	1.31	2.06
P3/20 s	1.82	2.55



(a) (b)

Figure 6. Weight change of the PVA samples with time of immersion: (a) swelling and (b) solubility.

dominates, swelling increases and solubility decreases. If chain scission dominates, then solubility increases and swelling decreases.

CONCLUSIONS

The exposure time effects on ATR FT-IR features, roughness, surface chemical structure, weight loss, and degree of swelling of the PVA films were examined and the results were correlated. The changes in shape, size, and intensity of the peaks in ATR FT-IR and XPS spectra have evidenced the surface structure modifications. Both chain scissions and cross-linkings appear as a result of atmospheric plasma treatment of PVA film. After the plasma treatment of the polymeric surfaces, we observed that the atomic fraction of oxygen content increases, while for carbon it decreases. This is also proof that the surface, after the plasma treatment, is more oxidized. It can be seen from the XPS analysis and the AFM measurements of the PVA samples that even a short plasma treatment (10 s) is suitable for changing the surface.

REFERENCES

1. Ngawhirunpat, T., P. Opanasopit, T. Rojanarata, P. Akkaramongkolporn, U. Ruktanonchai, and P. Supaphol. 2009. Development of meloxicam-loaded electrospun polyvinyl alcohol mats as a transdermal therapeutic agent. *Pharm. Dev. Technol.* 14: 70–79.
2. Kim, J. O., J. K. Park, J. H. Kim, S. G. Jin, C. S. Yong, D. X. Li, J. Y. Choi, J. S. Woo, B. K. Yoo, W. S. Lyoo, J. A. Kim, and H. G. Choi. 2008. Development of polyvinyl alcohol–sodium alginate gel-matrix-based wound dressing system containing nitrofurazone. *Int. J. Pharm.* 359: 79–86.
3. Han, S. E., and I. S. Hwang. 2002. Modeling of the optical anisotropy of a dye polarizer. *J. Polym. Sci. Polym. Phys.* 40: 1363–1370.
4. Taepaiboon, P., U. Rungsardthong, and P. Supaphol. 2006. Drug-loaded electrospun mats of poly(vinyl alcohol) fibres and their release characteristics of four model drugs. *Nanotechnology* 17: 2317–2329.

5. Morita, R., R. Honda, and Y. Takahashi. 2000. Development of oral controlled release preparations, a PVA swelling controlled release system (SCRS). I. Design of SCRS and its release controlling factor. *J. Control. Release* 63: 297–304.
6. Pawde, S. M., and K. Deshmukh. 2008. Characterization of polyvinyl alcohol/gelatin blend hydrogel films for biomedical applications. *J. Appl. Polym. Sci.* 109: 3431–3437.
7. Peng, S., Z. Gao, J. Sun, L. Yao, and Y. Qiu. 2009. Influence of argon/oxygen atmospheric dielectric barrier discharge treatment on desizing and scouring of poly (vinyl alcohol) on cotton fabrics. *Appl. Surf. Sci.* 255: 9458–9462.
8. De Geyter, N., R. Morent, C. Leys, L. Gengembre, and E. Payen. 2007. Treatment of polymer films with a dielectric barrier discharge in air, helium and argon at medium pressure. *Surf. Coat. Technol.* 201: 7066–7075.
9. Borcia, G., C. A. Anderson, and N. M. D. Brown. 2004. The surface oxidation of selected polymers using an atmospheric pressure air dielectric barrier discharge. Part I. *Appl. Surf. Sci.* 221: 203–214.
10. Matthews, S. R., M. G. McCord, and M. A. Bourham. 2005. Poly(vinyl alcohol) desizing mechanism via atmospheric pressure plasma exposure. *Plasma Process. Polym.* 2: 702–708.
11. Cai, Z., and Y. Qiu. 2006. The mechanism of air/oxygen/helium atmospheric plasma action on PVA. *J. Appl. Polym. Sci.* 99: 2233–2237.
12. Rafik, M., A. Mas, M. F. Guimon, C. Guimon, A. Elharfi, and F. Schue. 2003. Plasma-modified poly(vinyl alcohol) membranes for the dehydration of ethanol. *Polym. Int.* 52: 1222–1229.
13. Upadhyay, D. J., and N. V. Bhat. 2004. Pervaporation studies of gaseous plasma treated PVA membrane. *J. Membr. Sci.* 239: 255–263.
14. Yang, S. Y., and C. Y. Huang. 2008. Plasma treatment for enhancing mechanical and thermal properties of biodegradable PVA/starch blends. *J. Appl. Polym. Sci.* 109: 2452–2459.
15. Nastuta, A. V., G. B. Rusu, I. Topala, A. S. Chiper, and G. Popa. 2008. Surface modifications of polymer induced by atmospheric DBD plasma in different configurations. *J. Optoelectron. Adv. Mater.* 10 (8): 2038–2042.
16. Dumitrascu, N., G. Borcia, N. Apetroaei, and G. Popa. 2002. Roughness modification of surfaces treated by a pulsed dielectric barrier discharge. *Plasma Sources Sci. Technol.* 11: 127–134.
17. Kumar, A. C., and A. K. Mishra. 2007. 1-Naphthol as an excited state proton transfer fluorescent probe for sensing bound-water hydration of polyvinyl alcohol. *Talanta* 71: 2003–2006.
18. Borcia, G., C. A. Anderson, and N. M. D. Brown. 2006. Surface treatment of natural and synthetic textiles using a dielectric barrier discharge. *Surf. Coat. Technol.* 201: 3074–3081.
19. Gohil, J. M., A. Bhattacharya, and P. Ray. 2006. Studies on the cross-linking of poly(vinyl alcohol). *J. Polym. Res.* 13: 161–169.
20. Feng, X. S., M. X. Yu, H. G. Liu, D. J. Qian, and J. Mu. 2000. Studies on the composite Langmuir-Blodgett films of tetracationic porphyrazine cobalt and methyl orange. *Langmuir* 16: 9385–9389.
21. Pal, K., A. K. Banthia, and D. K. Majumdar. 2007. Biomedical evaluation of polyvinyl alcohol–gelatin esterified hydrogel for wound dressing. *J. Mater. Sci. Mater. Med.* 18: 1889–1894.
22. Helfand, M. A., J. B. Mazzanti, M. Fone, and R. H. Reamey. 1996. Effect of acetate distribution on surface segregation in poly(vinyl alcohol-*co*-vinyl acetate) copolymer films. *Langmuir* 12: 1296–1302.
23. Clarke, J. T., and E. R. Blout. 1946. Nature of the carbonyl groups in polyvinyl alcohol. *J. Polym. Sci.* 1 (5): 419–428.
24. Olabisi, O. 1997. *Handbook of Thermoplastics*. New York: Marcel Dekker, p. 272.

25. Leroux, F., C. Campagne, A. Perwuelz, and L. Gengembre. 2008. Polypropylene film chemical and physical modifications by dielectric barrier discharge plasma treatment at atmospheric pressure. *J. Colloid. Interface Sci.* 328: 412–420.
26. Wong, K. K. H., J. L. Hutter, M. Zinke-Allmang, and W. Wan. 2009. Physical properties of ion beam treated electrospun poly(vinyl alcohol) nanofibers. *Eur. Polym. J.* 45: 1349–1358.
27. Morent, R., N. Geyter, C. Leys, L. Gengembre, and E. Payen. 2007. Study of the ageing behaviour of polymer films treated with a dielectric barrier discharge in air, helium and argon at medium pressure. *Surf. Coat. Technol.* 201: 7847–7854.
28. Bae, P. H., Y. J. Hwang, H. J. Jo, H. J. Kim, Y. Lee, Y. K. Park, J. G. Kim, and J. Jung. 2006. Size removal on polyester fabrics by plasma source ion implantation device. *Chemosphere* 63: 1041–1047.