

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Poly(Hydroxybutyrate-co-9% Hydroxyvalerate) Film Surface Modification by Ar, O₂, H₂O/O₂, H₂O, and H₂O₂ Plasma Treatment

A. Mas^a; H. Jaaba^a; F. Schue^a; A. M. Belu^b; C. Kassis^b; R. W. Linton^b; J. M. Desimone^b

^a Laboratoire de Chimie Macromoléculaire Université des Sciences et Techniques du Languedoc, Montpellier Cédex, France ^b Department of Chemistry CB #3290 Venable and Kenan Laboratories, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, USA

To cite this Article Mas, A. , Jaaba, H. , Schue, F. , Belu, A. M. , Kassis, C. , Linton, R. W. and Desimone, J. M.(1997) 'Poly(Hydroxybutyrate-co-9% Hydroxyvalerate) Film Surface Modification by Ar, O₂, H₂O/O₂, H₂O, and H₂O₂ Plasma Treatment', *Journal of Macromolecular Science, Part A*, 34: 1, 67 – 79

To link to this Article: DOI: 10.1080/10601329708014935

URL: <http://dx.doi.org/10.1080/10601329708014935>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

POLY(HYDROXYBUTYRATE-*co*-9% HYDROXYVALERATE) FILM SURFACE MODIFICATION BY Ar, O₂, H₂O/O₂, H₂O, AND H₂O₂ PLASMA TREATMENT

A. MAS,* H. JAABA, and F. SCHUE

Laboratoire de Chimie Macromoléculaire
Université des Sciences et Techniques du Languedoc
34095 Montpellier Cédex 05, France

A. M. BELU, C. KASSIS, R. W. LINTON, and
J. M. DESIMONE

Department of Chemistry CB #3290 Venable and Kenan
Laboratories
University of North Carolina at Chapel Hill
Chapel Hill, North Carolina 27599-3290, USA

ABSTRACT

We modified poly(hydroxybutyrate-*co*-9% hydroxyvalerate) film surfaces with Ar, O₂, H₂O/O₂, H₂O, and H₂O₂ vapor plasma treatments. We measured the grafted oxygen concentration by XPS analyses and the wettability by a $\theta_{\text{H}_2\text{O}}$ contact angle method. Comparison between these various plasma treatments seems to indicate a better surface wettability correlated to C—OH bonds obtained with H₂O and H₂O₂ plasma than with Ar and O₂ plasma which incorporate oxygen atoms in C=O bonds more easily.

INTRODUCTION

Cold plasma treatments with low pressure gas have long been used to modify surface properties and roughness of polymer materials. Usual practical applications are found in the microelectronics industry, in improvement of surface adhesion, in membrane permselectivity optimization, and in compatibility of materials with living tissue [1]. Among the nonpolymerizable gas plasmas which are usually carried out, argon plasma particularly induces materials' cleaning and surface pretreatment. Also, argon can be used as carrying gas in a gas mixture plasma. On the contrary, the aggressiveness of oxygen plasmas lead to etching properties as well as an easy functional grafting which causes an increase in the surface hydrophilicity.

Water-vapor plasma is relatively less often used although it adds low cost, easy use, and its functional grafting capacity was unexpected, for example, in the case of a polysulfone membrane [2]. Water-vapor plasma was also used to increase the wettability of poly(methyl methacrylate) [3], a poly(etherurethane) film surface [4], and to promote cell adhesion and growth onto various polymer surfaces [5] as well as metal-polypropylene [6] and metal-polyimide [7] adhesion. Furthermore, its etching and cleaning properties were reported for one occasion [8, 9].

On the other hand, hydrogen peroxide vapor plasma was never studied, to our knowledge, within surface modification, and it would be interesting to determine its possibilities.

Plasma treatment is especially carried out with biomaterials to enhance biocompatibility properties and to deduce a relationship with the surface energy. Polyhydroxyalcanoate material shows two exceptional biocompatibility and biodegradability properties [10]; however, only a few studies have been dedicated to its plasma surface modification. In a previous report [11] we showed that no biocompatibility alteration is obtained when a fluorocarbon layer of about $17 \text{ mN} \cdot \text{m}^{-1}$ is deposited onto polyhydroxybutyrate (PHB) membranes.

For the present report we selected the copolymer poly(hydroxybutyrate-co-9% hydroxyvalerate) [P(HB-co-9% HV)] whose mechanical properties are better than those of PHB homopolymer.

In order to modify a P(HB-co-9% HV) film surface and to increase the surface energy, we used argon, oxygen, an oxygen-hydrogen peroxide mixture, and hydrogen peroxide plasma. The plasma parameters study permitted us to select the treatment which gives the best increase in wettability. The corresponding samples were analysed by XPS. We will study the biocompatibility of P(HB-co-9% HV) films in another report.

EXPERIMENTAL SECTION

Bacterial P(HB-co-9% HV), $M_w = 564,600$, was supplied by ICI. It was purified by dissolution in chloroform (CHCl_3) and precipitation in diethylether. A 10 wt% polymer solution in CHCl_3 was cast on a glass plate. After solvent evaporation, films were dried at 100°C for 48 hours and kept in a dry atmosphere. Contact angles of the film surfaces were measured with a Kruss G1 apparatus 5 seconds after the drop was deposited to avoid evaporation or absorption. Each given contact angle value is the average of 10 measurements; the static method was used. By using water

and α -bromonaphthalene, the Owens method [12] permitted us to calculate the surface energy γ_s and its dispersive γ_s^d and polar γ_s^p components. The scanning electron micrographs were taken with a Jeol 6300F with two magnifications, 2000 and 20,000.

XPS analyses were conducted on these films using a Perkin-Elmer Physical Electronic model 5400 spectrometer. Samples were irradiated using the $MgK\alpha$ x-ray source operated at 15 keV and 30 W. All binding energies have been charge corrected to 285.0 eV for polymeric aliphatic carbon.

The process followed and the experimental set-up used for the plasma treatments are described in a previous report [11]. The polymer samples were treated with a radio frequency (RF = 13.56 Mz) glow discharge plasma-generating apparatus. The plasma treatment was performed in a glass bell-jar type reactor containing two parallel plate electrodes and whose capacity is about 2.5 L. After the reactor was degassed, the samples were exposed to the plasma for given times and powers. The oxygen flow was continued for 10 minutes and then the system was again degassed for 20 minutes. We verified that P(HB-co-9% HV) films do not absorb water or hydrogen peroxide with identical pressure and time conditions with those of plasma treatment without glow discharge. Indeed, the contact angle was not modified when the power was turned off.

RESULTS AND DISCUSSION

The comparison of data in Tables 1, 2, and 3 concerning the effects of various treatment parameters on the wettability shows the decrease of θ_{H_2O} contact angle values with relatively short times of plasma treatment; it is lower than 5 minutes in

TABLE 1. Different Argon and Oxygen Plasma Treatments and Contact Angle ($\theta_{H_2O} \pm 1^\circ$) of a P(HB-co-9% HV) Treated Surface. Contact Angle of the Nontreated surface: 71°

Plasma treatment parameters			Contact angle θ_{H_2O} degrees just after treatment	
Power (W)	Pressure (Pa)	Time	Argon plasma	Oxygen plasma
45	50	40 s	49	45
"	"	3 min	52	41
"	"	5 min	52	41
"	"	15 min	55	48
"	"	25 min	59	48
"	"	30 min	59	49
75	50	40 s	51	40
"	"	3 min	55	40
"	"	5 min	57	41
"	"	15 min	55	41
"	"	25 min	42	40
"	"	30 min	42	40

TABLE 2. Different Water and Hydrogen Peroxide Plasma Treatments and Contact Angle ($\theta_{\text{H}_2\text{O}} \pm 1^\circ$) of a P(HB-co-9% HV) Treated Surface. Contact Angle of the Nontreated Surface: 71°

Plasma treatment parameters			Contact angle $\theta_{\text{H}_2\text{O}}$ degrees just after treatment	
Power (W)	Pressure (Pa)	Time	H ₂ O plasma	H ₂ O ₂ plasma
45	100	40 s	55	38
"	"	5 min	43	41
"	"	10 min	42	41
"	"	15 min	42	43
"	"	25 min	50	46
"	"	30 min	52	46

TABLE 3. Different Plasma Treatment Parameters of Water/Oxygen Mixture and Contact Angle ($\theta_{\text{H}_2\text{O}} \pm 1^\circ$) of a P(HB-co-9% HV) Treated Surface. Contact Angle of the Nontreated Surface: 71°

Plasma treatment parameters			Contact angle $\theta_{\text{H}_2\text{O}}$ degrees just after treatment:
Power (W)	Pressure (Pa)	Time	H ₂ O/O ₂ mixture plasma
45	100/150	40 s	40
"	"	3 min	41
"	"	5 min	37
"	"	15 min	39
"	"	20 min	40
"	"	25 min	42
"	"	30 min	40
75	100/150	40 s	41
"	"	3 min	42
"	"	5 min	45
"	"	20 min	43
"	"	25 min	41
"	"	30 min	40

the case of O_2 , H_2O , H_2O_2 , and O_2/H_2O plasmas. This result is shown more effectively in Figs. 1, 2, 3, and 4. Only the argon plasma needs a 30-minute time treatment. The lowest θ_{H_2O} values are obtained with the H_2O_2 plasma ($\theta_{H_2O} = 38^\circ$) and the O_2/H_2O plasma ($\theta_{H_2O} = 37^\circ$). The power increase from 45 to 75 W has a negligible effect on the H_2O/O_2 plasma while it gives a weaker θ_{H_2O} value with Ar and O_2 plasmas.

The greatest surface energy values (γ_s) and the corresponding dispersive and polar components (γ_s^d and γ_s^p , respectively) as measured just after each kind of plasma treatment are listed in Table 4. The study of wettability evolution with storage time at ambient temperature (Tables 5 and 6) shows that θ_{H_2O} values increase for each kind of treatment. However, some weeks after treatment the stabilized value is lower than the nontreated film θ_{H_2O} value. Also, the polar component of the surface energy γ_s^p decreases. It was essentially responsible for the γ_s increase just after plasma treatment because the variations of the dispersive component γ_s^d remain rather weak. Only the surface energy evolution of argon and oxygen plasma-treated film is given (Table 5). Likewise, water/hydrogen peroxide and water/oxygen plasmas lead to a similar effect.

XPS analysis permitted the assignment of binding energies according to the indicated structure of the nontreated P(HB-co-9% HV) film surface (Table 7) and of the O_2 treated one (Table 8). Oxygen plasma treatment leads to an increase in the O/C atomic ratio corresponding to one additional oxygen for four monomer units: $O-CHR-CH_2-CO$, which is incorporated mostly as a $C=O$ bond. These results are explained in greater detail in our previous report [13]. No increase in O/C is

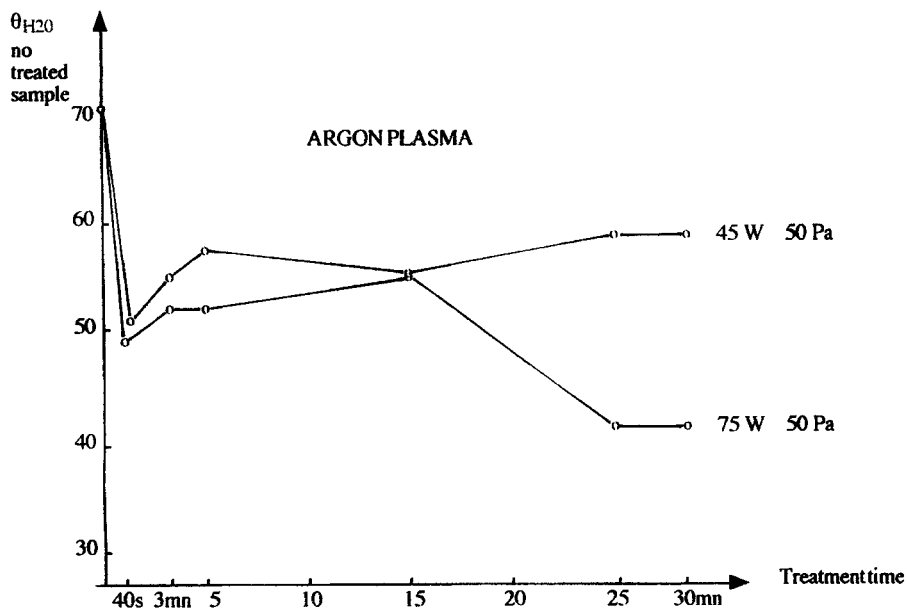


FIG. 1. Argon-plasma-treated P(HB-co-9% HV) film surface. Influence of treatment time on contact angle θ_{H_2O} value ($\pm 1^\circ$).

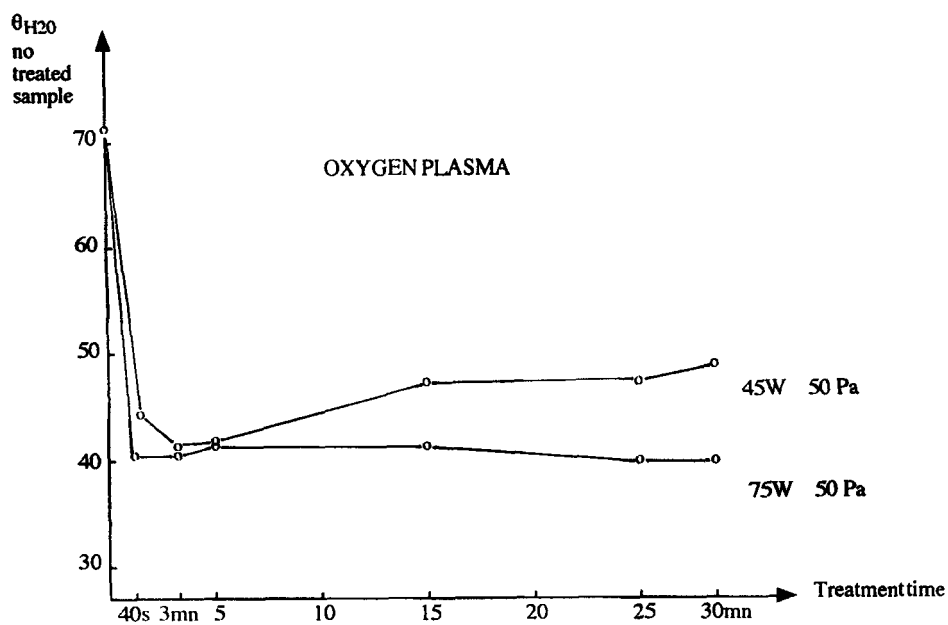


FIG. 2. Oxygen-plasma-treated P(HB-co-9% HV) film surface. Influence of treatment time on contact angle θ_{H_2O} value ($\pm 1^\circ$).

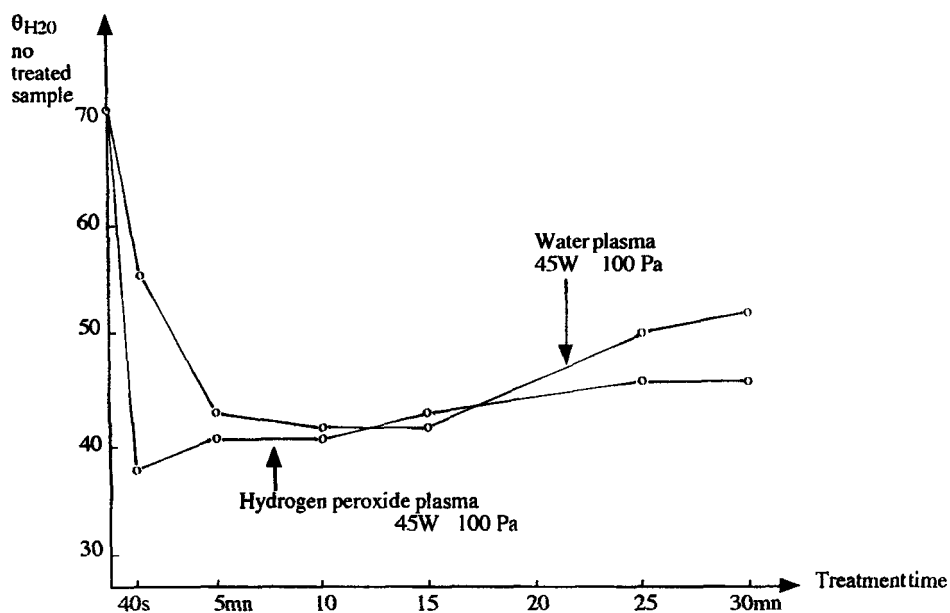


FIG. 3. Water- and hydrogen-peroxide-plasma treated P(HB-co-9% HV) film surface. Influence of treatment time on contact angle θ_{H_2O} value ($\pm 1^\circ$).

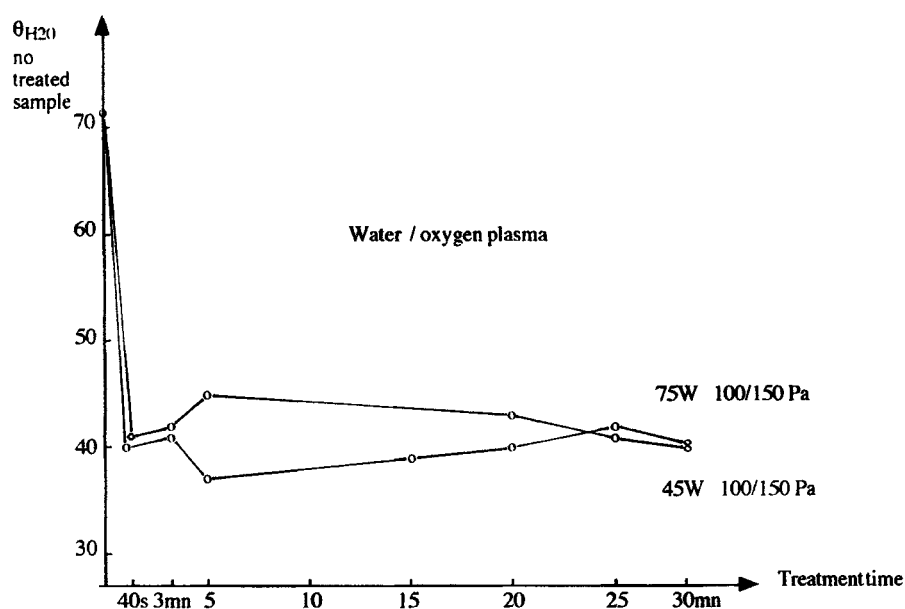


FIG. 4. Water/oxygen-plasma-treated P(HB-co-9% HV) film surface. Influence of treatment time on contact angle θ_{H_2O} value ($\pm 1^\circ$).

TABLE 4. Surface Energy γ_s , Dispersive γ_s^d , and Polar Components γ_s^p ($\pm 1 \text{ mN}\cdot\text{m}^{-1}$) of Various Plasma-Treated P(HB-co-9% HV) Film Surfaces Just after Treatment (Day 1)

Plasma treatment	γ_s	γ_s^d	γ_s^p
Argon	57.9	38.8	19.1
Oxygen	63.5	42.5	21
Water	65.1	42.9	22.2
Hydrogen peroxide	63.8	39.5	24.3
Water/oxygen	66.7	41.1	25.6
Nontreated sample	48.5	42.2	6.3

TABLE 5. Water Contact Angle $\theta_{\text{H}_2\text{O}}$ Values ($\pm 1^\circ$), Surface Energy γ_s , Dispersive γ_s^d , and Polar Components γ_s^p ($\pm 1 \text{ mN}\cdot\text{m}^{-1}$) of Argon and Oxygen Plasma-Treated P(HB-co-9% HV) Film Surface with Storage Time at Ambient Temperature. Nontreated Film Values: $\theta_{\text{H}_2\text{O}} = 71^\circ$, $\gamma_s = 48.5 \text{ mN}\cdot\text{m}^{-1}$, $\gamma_s^d = 42.2 \text{ mN}\cdot\text{m}^{-1}$, and $\gamma_s^p = 6.3 \text{ mN}\cdot\text{m}^{-1}$. Day 1 Means 45 minutes after Plasma Treatment

Plasma treatment		Days after plasma treatment				
		1	10	20	50	90
Argon plasma						
75 W 50 Pa 40 s	$\theta_{\text{H}_2\text{O}}$	49	54	56	55	58
	γ_s	57.9	56.1	54.8	—	—
	γ_s^d	38.8	40.8	40.5	—	—
	γ_s^p	19.1	15.3	14.3	—	—
Oxygen plasma						
75 W 50 Pa 5 min	$\theta_{\text{H}_2\text{O}}$	40	45	48	59	62
	γ_s	63.5	61.8	62.3	53	—
	γ_s^d	42.5	41.9	45.6	40.2	—
	γ_s^p	21	19.9	16.7	12.8	—

TABLE 6. Water Contact Angle, $\theta_{\text{H}_2\text{O}}$, values ($\pm 1^\circ$) of Various Plasma-Treated P(HB-co-9% HV) Film Surfaces. Evolution with Storage Time at Ambient Temperature. Day 1 Means 45 minutes after Plasma Treatment

	Plasma treatment conditions			Days after plasma treatment			
	Power (W)	Pressure (Pa)	Time	1	10	20	30
H ₂ O	45	100	5 min	43	66	68	68
H ₂ O ₂	45	100	40 s	38	52	68	68
H ₂ O/O ₂	45	100/150	40 s	40	48	52	62
H ₂ O/O ₂	45	100/150	5 min	37	45	55	60
H ₂ O/O ₂	45	100/150	30 min	40	—	54	65
H ₂ O/O ₂	75	100/150	40 s	41	—	53	61
H ₂ O/O ₂	75	100/150	5 min	45	—	55	62
H ₂ O/O ₂	75	100/150	30 min	40	47	—	66
Nontreated film				71	71	71	71

TABLE 7. XPS Analysis of P(HB-co-9% HV). Take-off Angle: 70°. Binding Energy of C_{1s} and O_{1s} Functional Groups

$\left(\text{O}_f \text{C}_c \text{H} - \text{C}_b \text{H}_2 - \overset{\text{O}_e}{\parallel} \text{C}_d \right)_{0.91} - \left(\text{O}_f \text{C}_c \text{H} - \overset{\text{C}_a \text{H}_3}{\text{C}_a \text{H}_2} - \overset{\text{O}_e}{\parallel} \text{C}_d \right)_{0.09}$						
BE, eV	289.3	286.9	285.6	285	533.9	532.8
Functional group	C=O C _d	O—C C _c	CH ₂ C _b	CH ₃ C ₂ H ₅ C _a	O—C O _f	C=O O _e

obtained with argon plasma treatment for each take-off angle, 20 or 70°; moreover, we can see a weak carbon contamination.

Based on the data averaged from two samples, water and hydrogen peroxide vapor plasma treatments lead to an increase of the O/C ratio, corresponding respectively to an additional oxygen for approximately 10 and for 6 monomer units (Table 9). Ratios between the carbonyl C_{1s} or ether C_{1s} and the hydrocarbon C_{1s} components seem to show that oxygen is incorporated in the following O—C bond. This result is evidenced without ambiguity in the case of Sample 2. Although we cannot conclude definitively about an increase in the C=O bond, we suggest an hydroxyl group grafting which increases the ether C_{1s} value. Unfortunately, there is no direct evidence to prove this because the energy difference between a carbon atom bonded to an OH group ($E_{\text{C-OH}} = 286.1$ eV) and to an OC group ($E_{\text{C-OC}} = 286.4$ eV) is very weak. The O_{1s} spectrum deconvolution does not give more information.

The data analysis confirms the usual interpretation about the importance of the kind of gas on polymer surface modification. Argon plasma treatment of a P(HB-co-9% HV) film surface produces the thin cracks shown on the scanning electron micrographs (Fig. 5) and is associated with contamination. The functional groups grafted, which are characterized by the contact angle evolution, modify only the upper part of the polymer surface. The XPS depth analysis of about 2 nm with

TABLE 8. XPS Analysis of Nontreated, Ar, and O₂ Plasma-Treated P(HB-co-9% HV) Film Surface. O/C Ratio Evolution with Take-off Angle Values. The Values Shown Are the Average 3 Spots/Sample with an Atomic Percentage Standard Deviation from 0.08 to 1.40%.

	O/C ratio	
	Take-off angle: 20°	Take-off angle: 70°
Nontreated sample	0.44	0.46
Argon plasma	0.40	0.44
Oxygen plasma	0.52	0.55

TABLE 9. XPS analysis of Nontreated, H₂O, and H₂O₂ Plasma-Treated P(HB-co-9% HV) Film Surface. Take-off Angle 45°. Atomic Ratio Evolution (see Table 7 for symbols)

	Sample 1			Sample 2		
	O/C	C _d /C _a + C _b	C _c /C _a + C _b	O/C	C _d /C _a + C _b	C _c /C _a + C _b
Nontreated sample	0.49	0.43	0.52	0.51	0.41	0.47
H ₂ O plasma	0.53	0.50	0.53	0.56	0.42	0.53
H ₂ O ₂ plasma	0.58	0.46	0.55	0.56	0.41	0.58

a take-off angle of 20° may not permit detection of the new atomic groups which are responsible for the wettability improvement and are probably due to an oxygen-induced grafting because they are in very low concentration.

Oxygen plasma treatment has a more important effect on the film surface than does Ar plasma. The aggressiveness of the species created in the plasma phase (Reaction 1) causes polar groups to graft, causes etching, and creates some small aggregates (Fig. 5).



Generally, etching increases with power and time treatment. Therefore, in order to avoid etching, a few authors have used a flash discharge of 1/10 second [14]. Scanning electron microscopy does not conclusively show a surface etching with the water vapor plasma treatment. The C_c/C_a + C_b ratio increase (Table 9) may be interpreted according to Reaction (2) where OH* radicals appear and produce C—OH bonds on the polymer film surface.



A greater power would lead to etching by O* oxygen radical formation (Reaction 3):



Indeed, the presence of OH* and H* radical species in the water vapor plasma was demonstrated by optical emission spectroscopy. A correlation between contact angle, concentration of oxygen at the surface, and the intensity of the OH* radical was established [2].

Also, some effects of water vapor added to oxygen are an increase in atomic oxygen concentration and the production of OH* radical in the plasma [15] which gives a lower θ_{H_2O} contact angle value in the case of our polymer film (Figs. 2 and 4). Etching and grafting competition leads to classic curves with a minimum value of θ_{H_2O} for particular power and time values (Figs. 3 and 4).

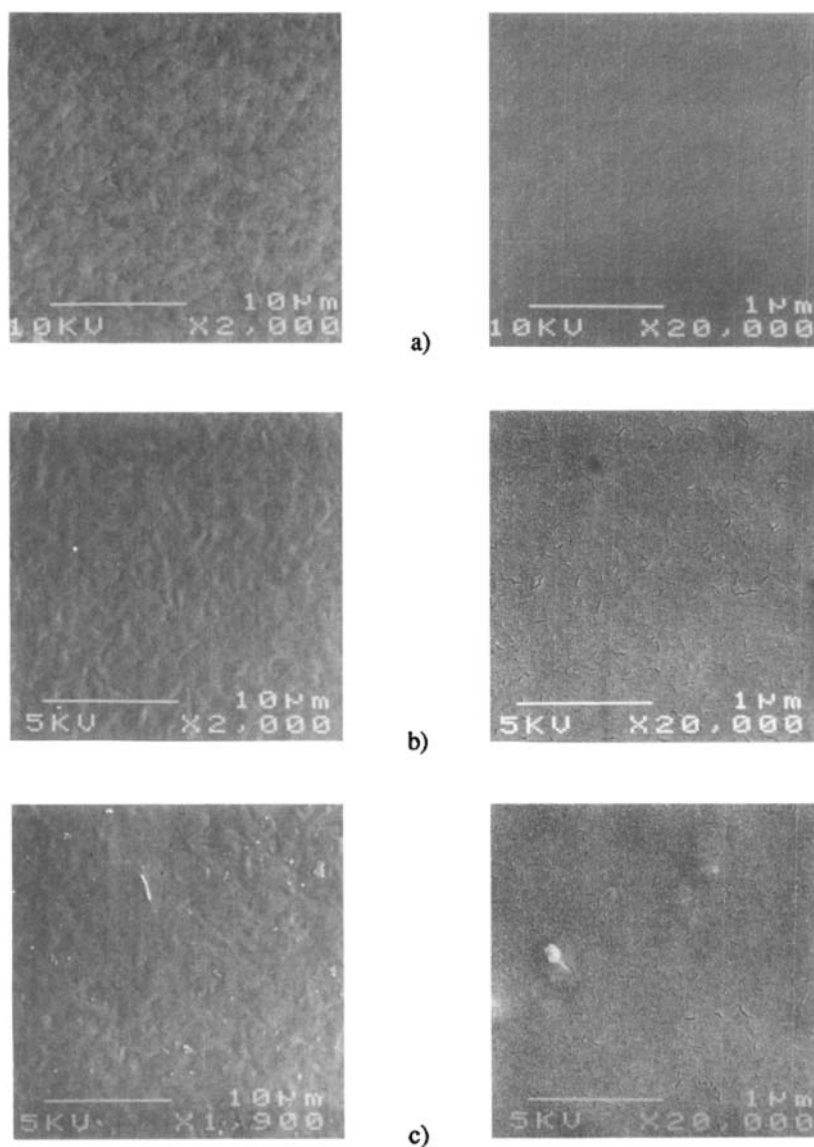


FIG. 5. Scanning electron micrographs (magnification 2000 \times and 20,000 \times of (a) nontreated P(HB-co-9%HV) film surface, (b) argon-plasma-treated sample, and (c) oxygen-plasma-treated sample.

These results can be applied to the hydrogen peroxide vapor plasma treatment which should create a more significant amount of OH* radicals (Reaction 4) than the water vapor plasma, so oxygen incorporation in C—OH bonds is greater.



The wettability lost during storage after all kind of plasma treatment is generally attributed to macromolecular chains motions [16] and buried polar groups in

the polymer bulk that minimize the interfacial energy. Although all of the results are difficult to interpret, it seems that the $\theta_{\text{H}_2\text{O}}$ values increase more rapidly with H_2O and H_2O_2 plasma treatments than with Ar , O_2 , or $\text{H}_2\text{O}/\text{O}_2$ ones (Table 6). This would be due to the easier movement of grafted macromolecules in relation to the kind of newly introduced polar groups. The weaker aggressiveness of the H_2O_2 plasma brings a minor perturbation of the crystalline state a few nanometers under the surface, and the delay for the modified chains to organize and attain equilibrium is shorter.

CONCLUSION

Wettability improvement of P(HB-co-9% HV) film surfaces can be obtained with Ar or O_2 plasmas and with the less used H_2O or H_2O_2 plasmas.

Ar and O_2 plasmas favor etching and increase the ease of oxygen atom incorporation which, in great part, is in $\text{C}=\text{O}$ bonds. However, H_2O and H_2O_2 plasmas increase the wettability more easily, with H_2O_2 being better than H_2O plasma with regard to $\theta_{\text{H}_2\text{O}}$ contact angle although the oxygen grafted is weaker. That would be related to the greater number of $\text{C}-\text{OH}$ bonds created, leading to the best surface hydrophilicity.

ACKNOWLEDGMENT

We gratefully acknowledge the financial support of the European Commission Brite-Euram (BRE 2 CT 920205).

REFERENCES

- [1] H. Biederman and Y. Osada, *Adv. Polym. Sci., Polym. Phys.*, **95**, 57 (1990).
- [2] K. Asfardjani, Y. Segui, Y. Aurelle, and N. Abidine, *J. Appl. Polym. Sci.*, **43**(2), 271 (1991).
- [3] T. G. Vargo and J. A. Gardella, *J. Polym. Sci., Part A, Polym. Chem.*, **27**, 1267 (1989).
- [4] T. G. Vargo and R. E. Baier, *Ibid.*, **29**, 535 (1991).
- [5] J. H. Lee, J. W. Park, and H. B. Lee, *Biomaterials*, **12**, 443 (1991).
- [6] H. Guezenoc, Y. Segui, S. Thery, and K. Asfardjani, *J. Adhes. Sci. Technol.*, **7**(9), 953 (1993).
- [7] R. D. Goldblatt, L. M. Ferreiro, and T. H. Chao, *J. Appl. Polym. Sci.*, **46**(12), 2189 (1992).
- [8] Y. Hiroshi and S. Keisute, Japanese Kokai Tokkyo Koho JP 01,112,734 (1989).
- [9] X. V. Ermokhin and I. M. Tokmulin, USSR Patent 1,421,249 (1992).
- [10] A. J. Anderson and E. A. Dawes, *Microbiol. Rev.*, p. 450 (1990).
- [11] F. Schue, G. Clarotti, J. Sledz, A. Mas, K. E. Geckeler, W. Gopel, and A. Orsetti, *Makromol. Chem., Macromol. Symp.*, **73**, 217 (1993).
- [12] D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, **13**, 1741 (1969).

- [13] A. Mas, H. Jaaba, F. Schue, A. M. Belu, C. Kassis, R. W. Linton, and J. M. Desimone, *Makromol. Chem. Phys.*, *197*, 2331 (1996).
- [14] J. F. Friedrich, W. Saur, and W. Unger, *Surf. Coat. Technol.*, *59*, 37 (1993).
- [15] S. Fujimura, K. Shinagawa, and M. Nakamura, *J. Vac. Sci. Technol.*, *B9*(2), 357 (1991).
- [16] H. Yasuda and A. K. Sharma, *J. Polym. Sci., Part B, Polym. Phys.*, *19*, 1285 (1981).

Received November 12, 1995

Revision received April 1, 1996