

Oxygen-Plasma-Treated Polypropylene Interfaces with Air, Water, and Epoxy Resins: Part I. Air and Water

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SYNOPSIS

Oxygen plasma treatment of polypropylene (PP) surfaces led to introduction of oxygen-containing functionalities, with consequent improvement of surface wettability. A combination of X-ray photoelectron spectroscopy (XPS), static secondary ion mass spectroscopy (SSIMS), and contact angle measurements (water-in-air and air-in-water) allowed us to characterize the behavior of the treated surface in contact with air (low-energy surface) and water (high-energy surface).

The treated surface showed the tendency to rearrange itself to minimize its interfacial energy. When contacted with air (low-energy surface), polar groups were buried away from the polymer/air interface, while in contact with water (high-energy surface) polar groups remained at the polymer/water interface.

When contacted with air, the polymer surface layer rearranged by macromolecular motions within itself, since interdiffusion with the bulk polymer seems forbidden. These motions are thermally activated and it was possible to obtain an apparent activation energy (58.1 kJ/mol) close to those reported for other vinyl polymers.

INTRODUCTION

Plasma treatments have long been known to increase the wettability of polyolefin surfaces.¹⁻⁵ Well known also is the fact that treated surfaces tend to lose wettability with time.^{1,6,7} In this respect, in the last few years an increasing amount of work has been devoted to polymer surface and interface dynamics.^{8,9}

The effect of flame treatments^{10,11} and electrical discharges or plasmas^{12,13} on the chemistry of polypropylene (PP) surfaces has been extensively studied in the past. In this work, a single and reproducible oxygen plasma treatment condition was chosen, focusing on the behavior with time of the treated surface in contact with media of different surface energy, namely air and water.

X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectroscopy (SSIMS) have been used to assess the surface composition of untreated and plasma-treated surfaces. In the case of SSIMS, the use of ¹⁸O₂ plasmas (for the first time, to our knowledge) provided unambiguous evidence on the oxygen plasma/surface interaction, free of contributions from contamination or other environmental effects. Water-in-air and air-in-water contact angle hysteresis measurements provided important information about the wettability and aging of treated surfaces in contact with different media. Fourier Transform Infrared in the Attenuated Total Reflectance mode (FTIR-ATR) and scanning electron microscopy (SEM) were used to detect eventual oxygen-plasma-induced changes in vibrational spectra and surface morphology, respectively.

A preliminary and partial account of the contact angle and XPS parts of this work was presented earlier.¹⁴ In part II of this work, we will discuss the properties of interfaces of untreated and oxygen-plasma-treated polypropylene surfaces with epoxy resins.¹⁵

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EXPERIMENTAL

Materials and Procedures

Oxygen plasma treatments were performed using a parallel plate reactor, with the samples located on the water-cooled grounded electrode. The plasma parameters were the following: excitation frequency, 13.56 MHz; power, 100 W; pressure, 2 Pa; gas flow, 8 cc (STP)/min; treatment time, 20 s. Oxygen from lecture bottles supplied by Carlo Erba was used. Isotactic polypropylene plaques (Himont SP179 grade) were used in the form of 25 × 100 mm strips.

For SSIMS studies some samples were treated with $^{18}\text{O}_2$ plasma. The enriched gas was provided by MSD (Merck Sharp and Dohme) with 99% isotopic purity. The plasma parameters were the same as for $^{16}\text{O}_2$ plasma. To discriminate between introduction of oxygen at the PP surface induced by the plasma itself or by reaction of atmospheric oxygen with active sites, samples treated with $^{16}\text{O}_2$ were aged for 1 h in $^{18}\text{O}_2$ atmosphere (pressure = 100 Pa) and vice versa.

To study wettability decay, plasma-treated samples were aged at different temperatures: 77, 293, 333, 363, 393, 413, and 428K. Contact angle measurements were performed after allowing the sample to reach room temperature in air. The time between extraction from the oven and contact angle measurement never exceeded 8 min; therefore, we can safely assume that surfaces probed by contact angles are representative of the aging temperature. Beside the treated sample, untreated polypropylene subjected to the same thermal treatment was characterized, checking in this way that the sample surface had reached room temperature and no thermal oxidation had occurred. Aging was also performed in doubly distilled and carefully deionized water (at 293K). Untreated samples underwent the same aging procedure for comparison purposes.

Contact angles were obtained by the sessile drop technique on a Ramé-Hart contact angle goniometer. Advancing and receding angles were obtained by increasing or decreasing the drop volume until moving the three-phase boundary over the surface. We kept the capillary pipette of the microsyringe immersed in the drop during the entire measurement, as described in ¹. The reported values are the average over at least 10 different measurements, performed in different parts of the sample surface. The typical error is $\pm 3\text{K}$.

Figure 1 shows schematically the analytical procedures we used. The first (water-in-air) consists of the conventional measurement of advancing and re-

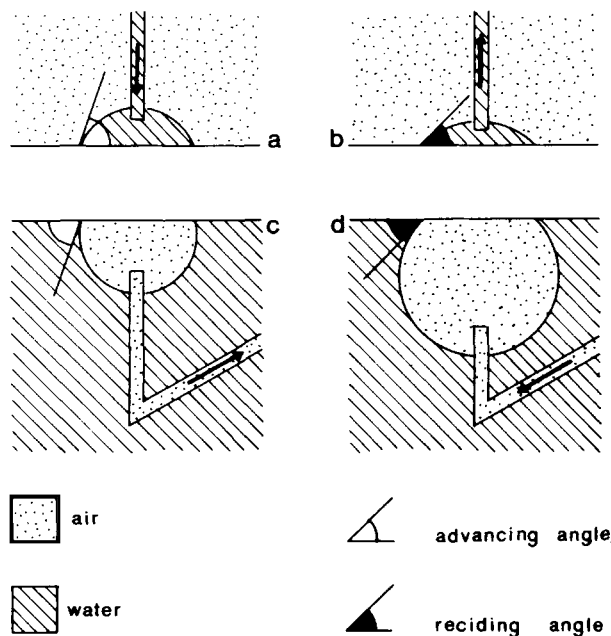


Figure 1 Schematic representation of water-in-air (a, b) and air-in-water (c, d) contact angle measurements.

ceding water contact angles in air, using carefully deionized and doubly distilled water [Figs. 1 (a) and (b)]. The second (air-in-water), followed the same procedure, but the advancing and receding contact angles of air in water “atmosphere” were measured, as shown in Figures 1 (c) and (d). The measurement of air-in-water contact angles allowed us also to observe that the rearrangement in water of plasma-treated surfaces is at least two orders of magnitude longer than water-in-air measurement times; therefore, it does not affect their interpretation. This was confirmed by water drop residence time-dependent water-in-air contact angle measurements, which showed that no change occurs for residence times up to 10 min.

XPS spectra were obtained using a PHI model 548 XPS spectrometer, with the experimental procedures extensively described in ¹⁰. SSIMS studies were performed using a VG quadrupole-based SIMSLAB instrument, with the procedures described elsewhere.¹¹

FTIR-ATR was performed using a Perkin-Elmer PE-1800 FTIR spectrometer. A germanium prism was used as an Internal Reflection Element (IRE) with a 45° incidence angle. In this experimental configuration, the thickness of the observed layer varies from about 0.3 μm at 3500 cm^{-1} to about 0.8 μm at 600 cm^{-1} .¹⁶

SEM micrographs were obtained using a Cambridge Stereoscan 604 microscope.

RESULTS

To limit the number of parameters, throughout this study we chose a single and reproducible plasma treatment condition. By SEM we checked that no significant morphological alterations were introduced on the PP surface by the treatment.

Water-in-Air Contact Angles

The first aim of this study is to clarify the behavior in air of oxygen-plasma-treated PP surfaces and in particular the effect of aging on wettability. For this purpose, we aged plasma-treated samples at different temperatures and characterized them by water-in-air contact angle measurements. Results are presented in Table I. Just after the treatment, the surface was much more wettable than untreated PP; with time, it tended to become again scarcely wettable.¹⁵

Advancing and receding angles behaved differently. The advancing angle decayed quickly, reaching as a limit the value of untreated PP. The receding angle remained fairly constant for a temperature-dependent time interval, then increased ultimately reaching a value lower than that of untreated PP. Figure 2 shows that the behavior of advancing and receding angles as a function of aging time [at 293K, Fig. 2(a)] is remarkably similar to the behavior predicted by various theoretical models¹⁷⁻¹⁹

for ideal heterogeneous surfaces composed of a high- and a low-energy part [Fig. 2(b)]. A change in composition of the layer determining contact angles is then suggested, in particular an increase in the low-energy (hydrocarbon) component and a decrease of the high-energy (oxidized) component. A fully nonpolar surface is not reached, as shown by the fact that receding angles do not converge completely with advancing angles and do not reach the value observed for untreated PP.

As to the temperature dependence, only at 77K no significant change in wettability was observed with time. For all other temperatures, decay of contact angles was observed. Furthermore, the decay rate increased with temperature. This evidence, together with the constancy found at 77K, points to thermally activated macromolecular motions responsible for aging.

XPS

Table II presents XPS data for samples aged under different conditions. As expected, a sizable amount of oxygen is introduced by the plasma treatments, but no particular changes were observed during aging in air and water, suggesting that the composition of the XPS-observed layer (some 5 nm) is essentially unaffected by aging. Figure 3 presents the line-fitted C-1s peaks relative to untreated [Fig. 3(a)] and plasma-treated PP, before [Fig. 3(b)] and after [Fig.

Table I Water-in-Air Advancing (a.a.) and Receding (r.a.) Contact Angles for Oxygen-Plasma-Treated PP as a Function of Aging Time and Temperature

Time (h)	293K		333K		363K		393K		413K	
	a.a.	r.a.	a.a.	r.a.	a.a.	r.a.	a.a.	r.a.	a.a.	r.a.
0.08	24	10			60	13	74	14	94	30
0.33	33	10	43	11	89	17	90	26	95	40
1.00	41	13	57	12	92	30	94	40	94	49
2.00			68	17	94	38	95	50	95	50
5.00	50	11			94	41				
7.00	52	11	92	30	95	40				
24.00	59	13	94	39	94	40				
27.00			94	40	95	40	94	50		
29.00	61	13								
86.50	72	12								
182.00	88	15								
230.00	92	32								
375.00	94	41								
720.00	95	40								

Untreated PP: a.a., 95; r.a., 80.

Treated PP, aged 375 h at 77K: a.a., 27; r.a., 10.

Treated PP, aged 2 h at 428K: a.a., 95; r.a., 55.

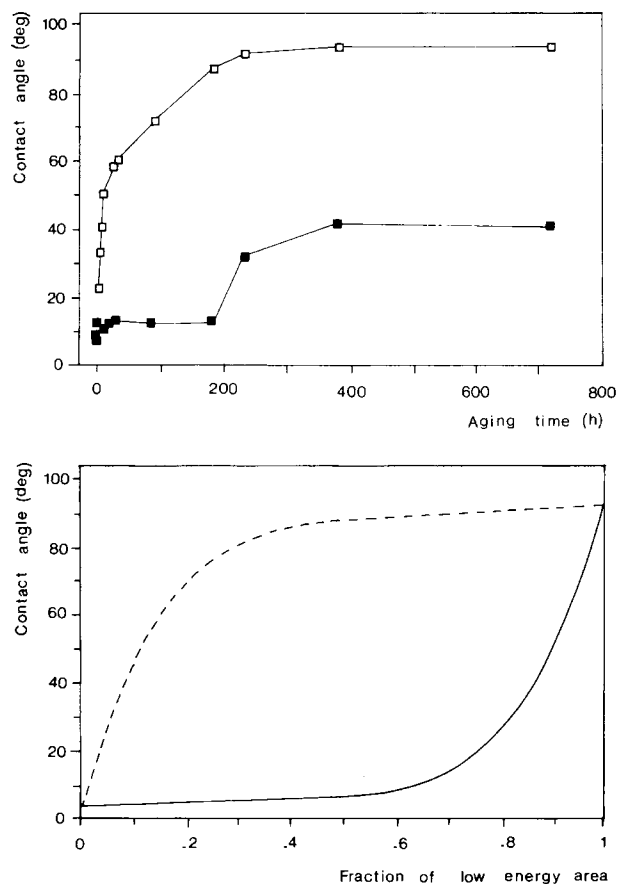


Figure 2 (a) Advancing (□) and receding (■) water contact angles as a function of aging time at 293K. (b) Theoretical behavior of an ideal heterogeneous surface (limiting angles 95° and 10°).

3(c)] aging in air. Oxygen plasma-treated samples have higher binding energy components related to oxygenated functions (C—OH, C=O, COOH) introduced by the treatment and, as previously ob-

Table II XPS Surface Composition of Oxygen-Plasma-Treated PP Surfaces, After Aging in Air at Different Temperatures

Sample	Surface composition (at. %)	
	C	O
Untreated	98.2	1.8
Just treated	84.2	15.8
Aged 24 h at 293K	84.9	15.1
Aged 375 h at 293K	85.0	15.0
Aged 27 h at 393K	85.6	14.4
Aged 375 h at 77K	85.1	14.9
Aged 8 h at 428K	84.8	15.2

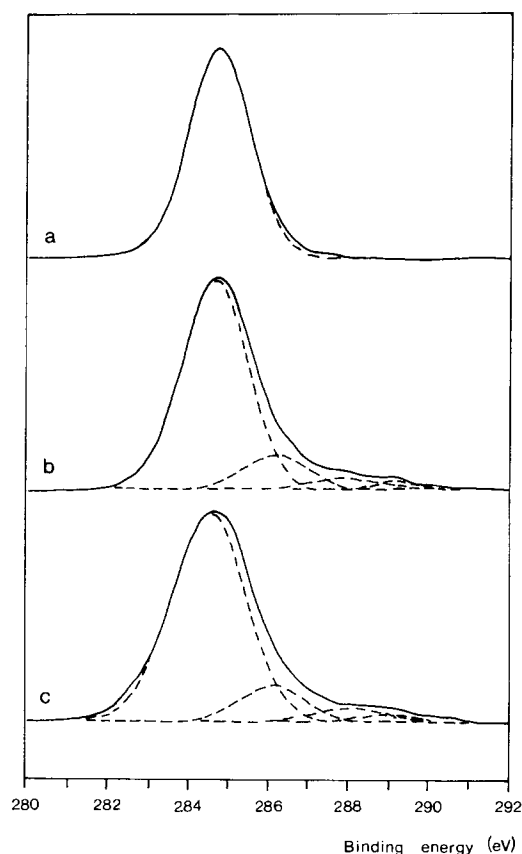


Figure 3 Line-fitted XPS C-1s peaks relative to (a) untreated PP, (b) oxygen-plasma-treated PP, immediately after treatment, (c) oxygen plasma treatment, aged 375 h at 293K.

served in the case of flame treatments, hydroxyl groups are most abundant among oxygen-containing functionalities formed after the treatment.¹⁰ Most important is the fact that, in agreement with the data of Table II, there is no significant change with aging, even if the corresponding contact angles are very different.

The simultaneous variation of contact angles and stability of XPS surface composition rule out the contribution of diffusion effects to surface reorganization. The latter is obtained by macromolecular motions within the modified layer.

FTIR-ATR

FTIR-ATR spectra did not show any difference between untreated and treated samples, both before and after aging. The reason is that, as observed earlier in the case of flame-treated PP,¹¹ the modified layer is not thick enough to induce detectable changes in ATR spectra.¹⁴

SSIMS

SSIMS allows us to obtain compositional information relative to a layer about 1 nm thick.^{20,21} It is therefore complementary to XPS and can be closely correlated to contact angle measurements, whose information is relative to a similar thickness.^{1,22} To draw comparisons between polymer surfaces of similar composition, Briggs et al.^{20,21} suggested the use of the ratio of the SSIMS intensities relative to O^- and CH^- ions (masses 16 and 13). We conformed to such a procedure, but to be completely sure that the observed oxygen derived only from the plasma treatment and not from contaminants, we treated some specimens with $^{18}O_2$ plasma. Furthermore, we used $CH^-/^{18}O^-$ instead of $^{18}O^-/CH^-$ ratios to convey more efficiently the obtainment of an increasingly apolar surface. Table III we presents $CH^-/^{18}O^-$ ratios for treated PP samples aged in different conditions, along with water-in-air contact angles obtained after identical aging. Contrary to what was observed by XPS, there is a dependence of SSIMS results on aging conditions, due to the lower observed depth (about 1 nm vs. about 5 nm in the case of XPS).

Figure 4 presents negative ion SSIMS spectra relative to $^{18}O_2$ plasma-treated PP, 16 h after the treatment, $^{18}O_2$ plasma-treated PP, after equilibration (2 h at 393K and 23 h at 293K), and untreated PP. The introduction of ^{18}O is clearly shown by the peaks at 18 and 19 amu ($^{18}O^-$ and $^{18}OH^-$, respectively). ^{16}O is present, as shown by the peaks at 16 and 17 amu ($^{16}O^-$ and $^{16}OH^-$, respectively). It may come from contaminants—some $^{16}O_2$ leaked into the reactor, etc. Interestingly, even after equilibration of the surface at 393K, some $^{16}O^-$ and $^{18}OH^-$ are present in the SSIMS spectrum [Fig. 4 (b)].

Figure 5 plots advancing and receding water contact angles are vs. the SSIMS $CH^-/^{18}O^-$. It is in-

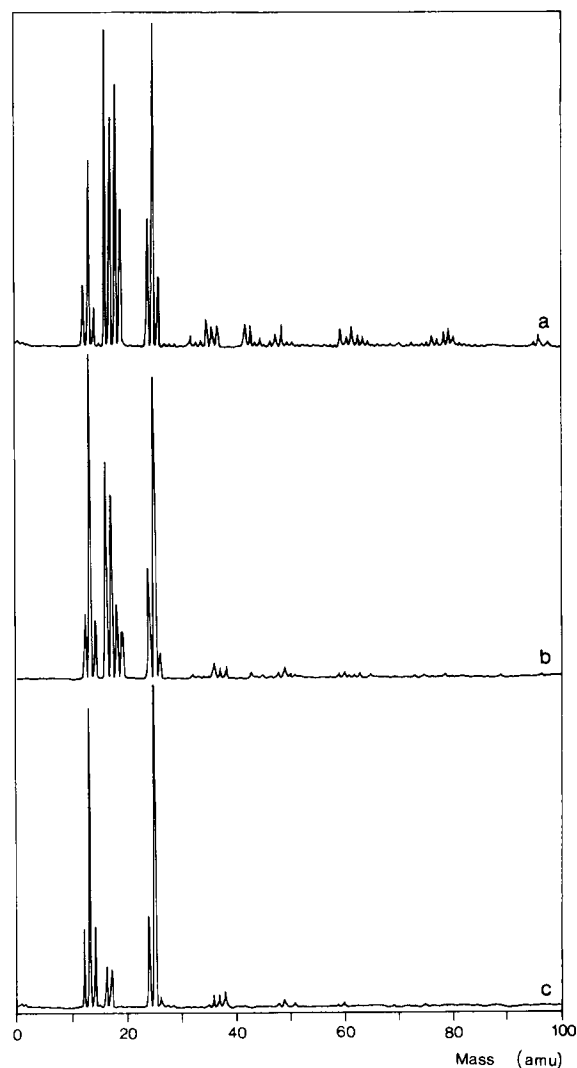


Figure 4 Negative ion SSIMS spectra of: (a) PP treated with $^{18}O_2$ plasma, aged 16 h at 293K; (b) PP treated with $^{18}O_2$ plasma, aged 2 h at 393K, 23 h at 293K; (c) untreated PP.

Table III SSIMS Negative Ion $CH^-/^{18}O^-$ (18 and 13 amu, respectively) Peak Intensity Ratios for Samples Aged in Different Conditions, Together with Water-in-Air Contact Angles Measured After Identical Aging

Aging Conditions	$CH^-/^{18}O^-$	a.a	r.a.
16 h, 293K	0.7	54	11
148 h, 293K	1.3	81	13
175 h, 293K	1.7	86	15
3 h, 333K; 44 h, 293K	2.9	92	30
2 h, 393K; 23 h, 293K	4.5	94	50

teresting to observe that the dependence of the advancing angle is close to that observed for advancing angles with time [Fig. 2 (a)] and foreseen theoretically for an ideal two-component surface [Fig. 2(b)]. The advancing angle follows immediately the introduction of a less wettable component at the surface, represented in our case by macromolecular motions leading to burial of oxygen-containing groups away from the surface and corresponding to an increase in the $CH^-/^{18}O^-$ ratio. Also, the receding angle follows the predicted behavior [Figs. 2 (a) and (b)]. It is relatively insensitive to the $CH^-/^{18}O^-$ ratio (and therefore to the amount of nonpolar component at the surface) up to a certain extent

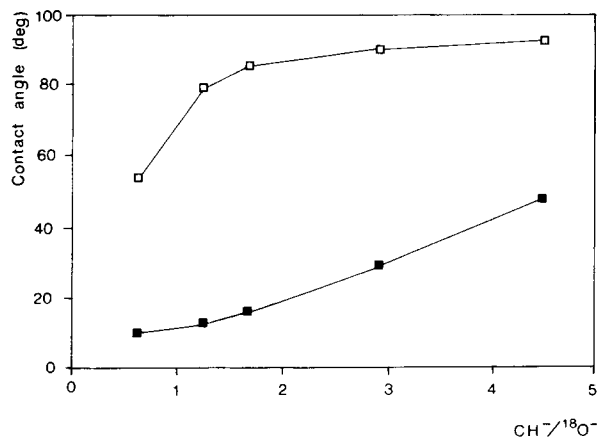


Figure 5 Advancing (\square) and receding (\blacksquare) contact angles as a function of SSIMS $^{18}\text{O}^-/\text{CH}^-$. The values are taken from Table I.

($\text{CH}^-/^{18}\text{O}^-$ close to 1.7) and increases only when the surface is poor in oxygen. The receding angle does not return to the value of untreated PP since macromolecular motions are not able to bury all functional groups away from the surface, as shown by the persistence of $^{18}\text{O}^-$ ions in the spectrum in Figure 4(b) and by the finite $\text{CH}^-/^{18}\text{O}^-$ ratio in Table III.

More Remarks Suggested by the Use of $^{18}\text{O}_2$ Plasmas

The availability of $^{18}\text{O}_2$ prompted us to contribute to the long-debated issue pertaining to whether the introduction of oxygen to the surface is only due to the plasma or partially to the interaction of the sample, when taken to air, with atmospheric oxygen.¹⁻³ Two samples, one treated with $^{18}\text{O}_2$ plasma and aged in $^{16}\text{O}_2$ and the other treated with $^{16}\text{O}_2$ plasma and aged in $^{18}\text{O}_2$, were analyzed by SSIMS. Their negative ion spectrum is shown in Figure 6. In the case of the sample treated in $^{18}\text{O}_2$ plasma and aged in $^{16}\text{O}_2$ [Fig. 6(a)], some ^{16}O is present, as shown by the peaks at 16 and 17 amu ($^{16}\text{O}^-$ and $^{16}\text{OH}^-$, respectively). This is not conclusive since, as mentioned earlier, it may come from contaminants—the $^{16}\text{O}_2$ leaked into the reactor, etc. The spectrum in Fig. 6(b) is more conclusive since there are no peaks at masses 18 and 19. So, at least for this particular treatment, the introduction of oxygen due to reactions of active sites with atmospheric oxygen seems negligible.

Air-in-Water Contact Angles

The combination of water-in-air contact angles, XPS, and SSIMS showed that the contact of a

plasma-treated surface with air, a low-energy surface, leads to macromolecular motions burying polar groups away from the surface and therefore reducing its wettability. Interfacing the same surface with a high-energy surface, such as water, changes reorganization patterns. Lavielle et al.^{23,24} studied the interaction between acrylic acid-grafted polyethylene and water and showed that polar groups are attracted to the surface by its contact with water.

We concurrently aged untreated, plasma-treated, and plasma-treated and equilibrated (2 h at 393°K) samples and measured their air-in-water contact angles as schematically shown in Figures 1(c) and (d). Advancing and receding air-in-water contact angles are presented in Table IV according to the convention suggested by Holly and Refojo.²⁵ Their meaning is similar to water-in-air contact angles.

Aging in water induced some changes of the wettability of untreated PP itself, suggesting some penetration of water in the polymer surface layer. From the data in Table IV, it is clear that interfacing the treated sample with a high-energy surface forbids the rearrangement of the polymer, thereby indicat-

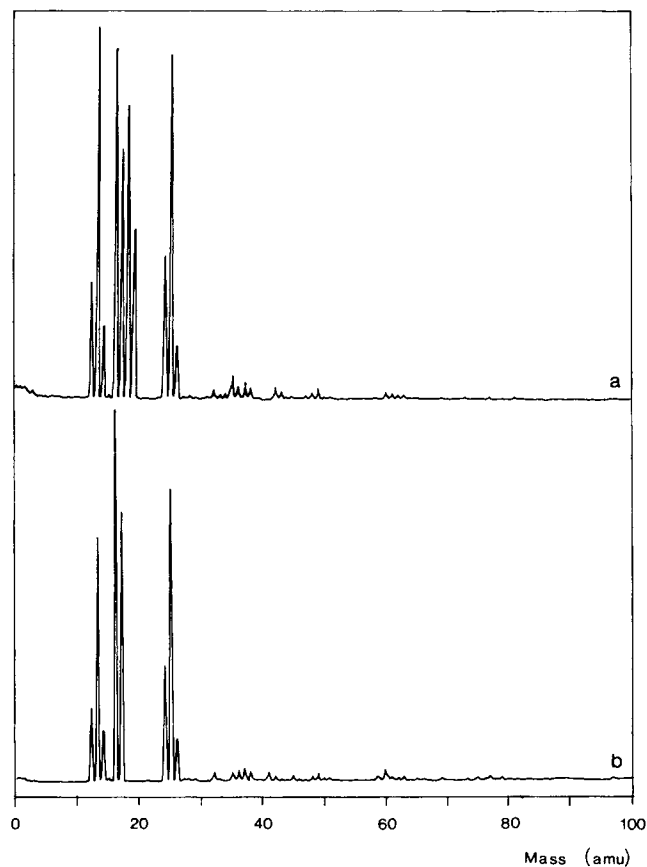


Figure 6 Negative ion SSIMS spectra of: (a) PP treated with $^{18}\text{O}_2$ plasma, aged in $^{16}\text{O}_2$; (b) PP treated with $^{16}\text{O}_2$ plasma, aged in $^{18}\text{O}_2$.

Table IV Air-in-Water Advancing (a.a.) and Receding (r.a.) Contact Angles for Untreated and Oxygen-Plasma-Treated PP as a Function of Aging Time in Water at 293K

Time (h)	Untreated PP		PP treated and immersed in water		PP, treated, equilibrated in air, then immersed in water	
	a.a.	r.a.	a.a.	r.a.	a.a.	r.a.
0.0	95	81	23	— ^a	95	48
1.0					95	49
2.0					92	44
5.0	96	78	23	— ^a		
24.0	95	75	23	— ^a	92	25
48.0	95	46	23	— ^a		
72.0	90	23	23	— ^a	23	— ^a
96.0	85	20	23	— ^a		
144.0	78	20	23	— ^a		

^a Close to zero, difficult to measure

ing that the surface tension is an important component of the global surface free energy driving to equilibrium the polymer surface after modification introduced, for instance, by plasma treatment. Moreover, aging a treated and equilibrated sample in water induces a surface that is identical to that observed for the sample treated and immediately immersed in water. On the other hand, if the sample aged in water is dried and aged in air, the water-in-air contact angles shown in Table V are obtained. The sample surface returns to a nonwettable situation, even if there is some difference both in timing and in extent of rearrangement, probably due to swelling by water.

XPS proved that the sample aged in water and reconditioned in air had the usual surface composition, therefore excluding extraction of low molec-

ular weight species by water (Table II). To be more confident in the above fact we also performed aqueous extraction tests.²⁶ The water drop used to measure contact angles on treated samples was reused on both treated and untreated samples, obtaining results identical to fresh drops, therefore excluding extraction effects.

Calculation of the Activation Energy for Macromolecular Motions

Due to the importance of macromolecular motions in controlling the response of the surface layer and the availability of temperature-dependent data for samples aged in air (Table I), we tried to evaluate their activation energy. We took as a reference the time needed to reach the advancing angle typical of untreated PP and on this basis straightforwardly calculated the Arrhenius plot in Figure 7. The linearity is very good and allowed us to obtain an apparent activation energy for macromolecular motions of 58.1 kJ/mol. The activation energies for surface relaxation in polyvinylchloride (PVC), polyvinylacetate (PVAc), and poly(vinylchloride-vinylacetate) (PVC-VAc) copolymers were reported.^{27,28} In the case of pure PVC and PVAc, it was 63 and 40 kJ/mol, respectively, while in PVC-VAc it was 43 kJ/mol, suggesting that in the latter case the motion of vinylacetate side chain is responsible for the observed value. Interestingly, in our case it is more of a main-chain motion problem, as in the case of PVC, and the observed value is also similar.

Table V Water-in-Air Advancing (a.a.) and Receding (r.a.) Contact Angles for Oxygen-Plasma-Treated PP Aged in Water (at 293K for 144 h) and Then Taken to Air

Time (h)	a.a.	r.a.
0.0	46	13
5.0	54	12
19.0	68	12
24.0	76	13
48.0	84	16
96.0	90	15
144.0	95	20
168.0	95	25
192.0	95	28

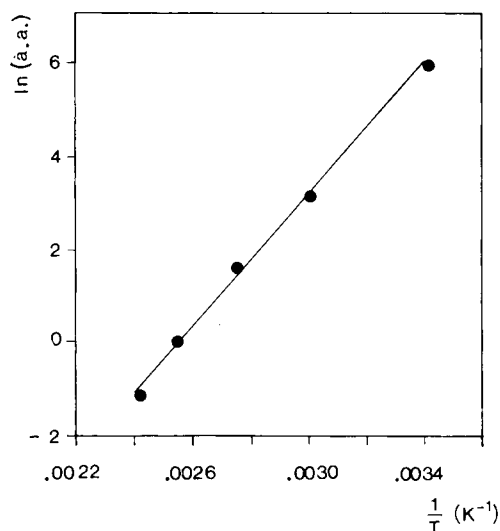


Figure 7 Arrhenius plot of the time needed to reach the advancing angle of untreated PP vs. temperature.

DISCUSSION

Plasma treatment of PP surfaces induces the introduction of oxygen-containing functionalities, as shown by both XPS and SSIMS. The modified layer thickness is close to the XPS observation depth. In fact, FTIR-ATR spectra have not been able to detect any treatment-induced alteration. The treatment itself is responsible for surface functionalization, while the interaction of active sites on the sample surface with atmospheric oxygen does not seem to be effective, as shown by SSIMS (Fig. 6). Among oxygen-containing groups, hydroxyls are the most abundant, as shown in XPS C-1s peaks (Fig. 3). The treated PP surface also becomes very wettable (Table I).

The surface, just after treatment, depending on the medium with which it is contacted, may or may not be close to equilibrium. Proximity to air, a low-energy surface, leads to rearrangements driven by the thrust to minimize interfacial energy,²⁹ i.e., minimizing the polymer surface tension (Tables I and V). When the contacted medium has a high-energy surface, such as water, the same principle, i.e., minimizing interfacial energy, blocks rearrangements of a just-treated (wetable) polymer surface and promotes them in a thermally equilibrated (nonwetable) one (Table IV).

A first corollary to these observations is that it is not really correct to talk about "polymer surfaces." Normally, what is studied is their interface with a low-energy surface, such as air or vacuum. It is anyway an interfacial problem. A second corollary is

that, to technologically overcome aging problems, a possible solution is to interface the treated specimen with a material having a high-energy surface, as suggested in some recent Japanese patents.^{30,31}

The mechanism of the reorganization of the modified surface layer is not diffusive, as shown by XPS, since the polar polymer formed at the surface is incompatible with bulk PP. Macromolecular motions within the surface layer (less than 5 nm thick) lead to minimization of the number of polar groups at the surface. However, this rearrangement is not complete, as shown by SSIMS and by the fact that while the advancing angle reaches the limiting value typical of untreated PP, the receding angle does not, indicating that some polar groups remain at the surface. Such a behavior is in agreement with the one expected from an ideal two-component heterogeneous surface, presented in Figure 2(b). To reach the advancing angle typical of the less polar component, a far less than complete coverage of the latter is sufficient. To obtain the convergence of the receding angle, a total coverage by the less polar component would be necessary. Such a phenomenon is unlikely if diffusion effects are not present, as in our case. The activation energy for rearrangement is typical of main chain motions and close to the value observed for PVC.^{26,27}

CONCLUSION

Plasma-treated PP samples are made of two distinct layers. The bulk is untreated PP. On top of it there is a layer, less than 5 nm thick, of what might be defined as a random copolymer, made of unaffected and oxidized units. This layer is immiscible with PP. After its formation by the treatment, it rearranges itself by thermally activated macromolecular motions, depending on the medium with which it is interfaced, to minimize the interfacial energy, which includes surface tension and chemical terms.

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