

Plasma Treatment of Polypropylene Surfaces: Characterization by Contact-Angle Measurements

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SYNOPSIS

Air plasma treatment has been used to introduce polar functional groups onto polypropylene surfaces to enhance the adhesion of coatings and paints. Plasma exposure times as well as the reaction medium (ambient, technical, and moistured technical air) have been varied. Time-dependent changes subsequent to the plasma treatment are monitored by contact-angle measurements. After short plasma exposures, the polar component of the surface energy is observed to decrease, to reach a minimum after ≈ 40 min. This behavior is interpreted in terms of a rotation of the introduced surface hydroperoxide groups into the interior of the polymer. This undesired loss in surface functionalization can be avoided by (a) increasing the treatment time in dry air, (b) use of moistured air as the reaction medium, or (c) posttreatment of the plasma-treated parts by water immersion. A plasma exposure of 120 s in dry air, followed by posttreatment in an aqueous medium at room temperature for 2–5 min, results in reproducible values of the surface energy σ , with polarities ($\sigma_{\text{polar}}/\sigma_{\text{total}}$) close to the desired value of $\approx 50\%$. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyolefins are extensively used materials for technical applications due to their low specific weight, adaptability to complicated structures, excellent solvent resistance, and availability at low cost. However, the poor wettability of polyolefin surfaces gives rise to problems when painting or metallization is required. To overcome these difficulties, various treatments have been suggested¹ with the aim of introducing polar groups into the polyolefin surface, such as flame treatment, chromic acid etching, or corona treatment.

Recently, plasma treatment^{2–6} has been introduced as a new technique for the modification of polymer surfaces. In this context, the term “plasma” is used in its general sense, to designate a partly ionized gas. Coopes and Gifkins⁷ reviewed the interaction of plasmas with polyethylene surfaces, for electron energies of 1–10 eV, electron densities varying between 10^9 and 10^{12} cm^{-3} , and typical plasma temperatures of ≈ 700 K. The modified

depth on the polymer surface was found to vary between 50 Å and 10 μm . Plasma treatment represents an effective and economic route for polymer surface modification.

Reactive gases such as O_2 (Ref. 7) or CF_4/O_2 mixtures,⁸ inert gases such as N_2 , He, or Ar, H_2 ,⁹ and, recently, CO_2 (Ref. 10) have been used as the plasma medium. Oxygen plasma was recently applied for the modification of polypropylene surfaces by Occhiello et al.¹¹ In the present report, the use of an air plasma is investigated as an efficient and cost-effective alternative. Contact-angle measurements are used to characterize the induced surface modification.

Detailed studies have been performed to elucidate the mechanism of plasma surface modification. Two effects are acting in parallel, i.e., the attack of the polymer by plasma species and the generation of radical sites in the polymer chains by the UV radiation associated with the plasma.⁹ Nitrogen incorporation from nitrogen atoms and ions in the plasma and surface oxidation by oxygen atoms and radicals are typical for the direct reaction of plasma species.^{9,12} Free radicals, detected in appreciable concentrations as a consequence of the UV radiation, undergo further reactions to form surface

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carbonyl and hydroxyl groups or give rise to cross-linking.¹²

EXPERIMENTAL

A. Pretreatment of the Plaques

From the received Euro-plaques (HIMONT, polypropylene type SP 179), plates of $4 \times 2 \text{ cm}^2$ size were cut and their edges smoothed. Subsequently, the plates were taken up with a pair of tweezers, washed with isopropanol three times, and dried in air. The dry plates were transferred into covered glass dishes (Petri dishes) to hold them free of dust up to the time of measurement. In all steps after the cleaning procedure, the plates were handled with a pair of tweezers to avoid contamination.

B. Plasma Treatment

The plates were transferred to the plasma chamber (Harrick, Model PDC-32G). The chamber was evacuated, flushed three times with the reaction gas to be used, and then evacuated to a pressure of 2 Pa. Three different atmospheres were used, i.e.: ambient air without any pretreatment, "technical air" from cylinders (Linde, 80% N_2 , 20% O_2 , free of CO_2 and trace gases), and moistured technical air.

After a stable pressure had been established, an inductively coupled plasma was generated in the chamber, using a radio-frequency of 13.56 MHz and a power of 100 W. Subsequent to the plasma treatment, the chamber was vented with the reaction gas. The instant of opening of the chamber was defined as the origin of the time scale for the subsequent measurements. The plaques were taken out of the chamber and transferred back to the covered glass dish. Within the Petri dish, a smaller vessel filled with water was placed to achieve a saturated water atmosphere.

C. Measurement of Contact Angles

Surface free energies, and of the corresponding polar and dispersive parts, have been determined according to the method described by Schultz et al.¹³ and summarized in Ref. 1, by measuring contact angles using various reference liquids. One minute before the measurement, the polypropylene plates were taken out of the storage vessel and inserted into the contact-angle instrument (Krüss, Model G-1). Ethylene glycol and bidistilled water were used as test fluids. This combination of liquids had been es-

tablished as the most appropriate one in earlier experiments. Other commonly used test fluids, such as diethyl phthalate and benzyl alcohol, turned out to be not suited for the present measurements. As a consequence of the low surface energy of the latter two liquids, which is smaller than the one of treated polypropylene, a complete spreading on the test plaques was observed.

Eight drops of each liquid were placed onto the surface of the plaque. The contact angle was determined on both sides of the drop in the Krüss instrument. Surface energies were calculated using the Krüss software. To divide the total surface energy into polar and dispersive components, the geometric mean method of Fowkes (cf. Ref. 1) was used. This procedure turned out to be suitable for representing small changes in the state of the surface. In contrast, the harmonic mean method of Wu¹ was found to be less useful, as it tends to level out small differences.

RESULTS

When investigating changes in the surface state subsequent to plasma treatment, it is important to recall the long lifetime ($\geq 100 \text{ h}$) of hydroperoxides introduced on the polypropylene surface by the plasma treatment. This exceedingly long reaction time may be altered by adding a posttreatment step subsequent to plasma exposure, in order to achieve a fast and directed decay of the hydroperoxides. Results obtained without and with such a posttreatment will now be presented in sequence.

A. Surface State after Plasma Exposure without Posttreatment

The measurements, performed over 4 h, characterize the initial stages of a reacting system. As a consequence of this fact, and because of heterogeneities that are unavoidably present on the surface of the technical plaques, the measurements are characterized by large statistical fluctuations. To obtain a representative set of data, each treatment was repeated and the time-dependent behavior measured three times. Averages and standard deviations determined from the three independent data sets are presented in the figures.

The effects of plasma treatment in three different reaction media (air, technical air, and moistured technical air) are compared as a function of the length of the treatment. Changes in surface energy are then followed as a function of measurement time after the treatment. Results are first reported for

changes in the surface energy occurring in the interval from 2 to 60 min after treatment; data obtained in the measurement time interval from 1 to 4 h are presented subsequently.

A.1. Changes Occurring during First Hour after Treatment

For a plasma exposure time of 90 s (Fig. 1), high values of the polar component of the surface energy (up to 32 mN/m) have been observed. The experimental standard deviations, shown in all figures as narrow bars superimposed on the average values, are high for most data in this series, such that we do not comment on the smaller excursions. However, at a measurement time of ≈ 40 min, a sharp decrease in the polar component is observed for the samples treated in ambient air and dry technical air.

The polarity, defined¹ as the ratio of the polar component to the total surface energy, $\sigma_{\text{polar}}/\sigma_{\text{total}}$, is presented in the lower part of Figure 1. As the total surface energy was found not to vary significantly as a function of measurement time, the de-

pendence of the polarity is here similar to the one of the polar component. Values between a maximum of > 0.7 and a minimum of 0.2 have been obtained.

When the treatment is extended to 120 s (Fig. 2), the fluctuations in the surface energies measured at different times appear reduced and the standard deviations are comparable for most measurements. The most uniform behavior as a function of measurement time is observed for the plaques treated in *moistured technical air*, for $t \geq 18$ min.

A further extension of the treatment to 150 s results in an increase in the polar component of the surface energy (Fig. 3). Measurements on the samples treated in *ambient air* exhibit large standard deviations; the treatment time appears to be too long and to result in nonuniform alterations of the surface for this gas mixture. The values of the surface energy observed after treatment in *dry technical air* exhibit a regular dependence on measurement time.

A treatment time of 180 s (Fig. 4) results in large fluctuations of the average surface energies for all three reaction media investigated. Standard deviations are often as large as the measured value itself.

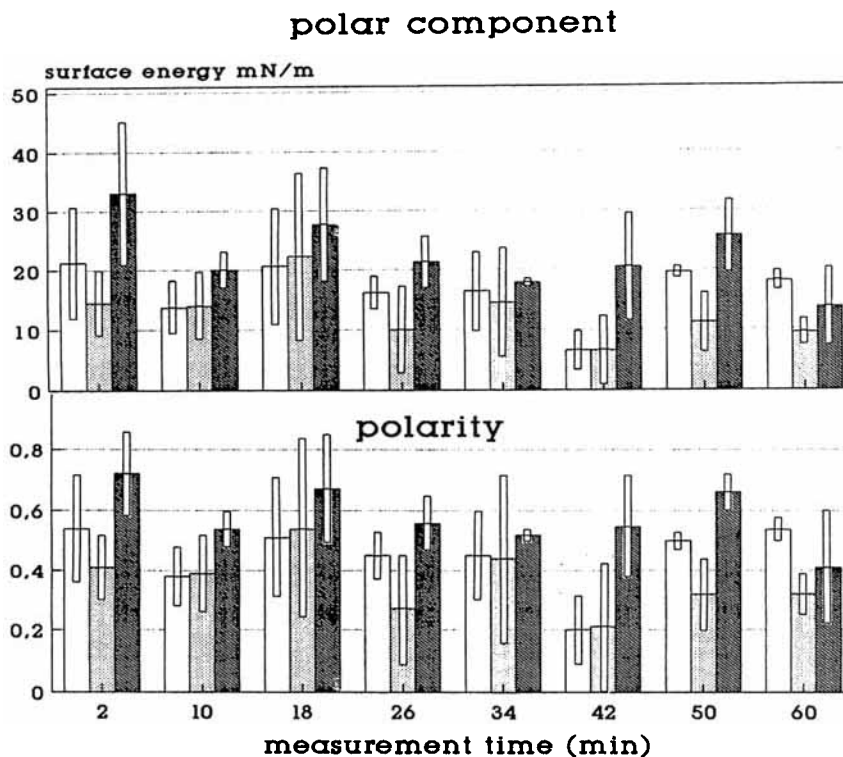


Figure 1 Air plasma treatment of polypropylene surfaces, using a 90 s plasma exposure time. Ambient air (white bars), dry technical air (shaded bars), and moistured technical air (dark bars) have been used as plasma media. Time-dependent changes in the polar component of the surface energy and of the polarity ($\sigma_{\text{polar}}/\sigma_{\text{total}}$) are followed as a function of time (2–60 min) after plasma exposure. Standard deviations are displayed on top of the averages in the form of narrow vertical bars.

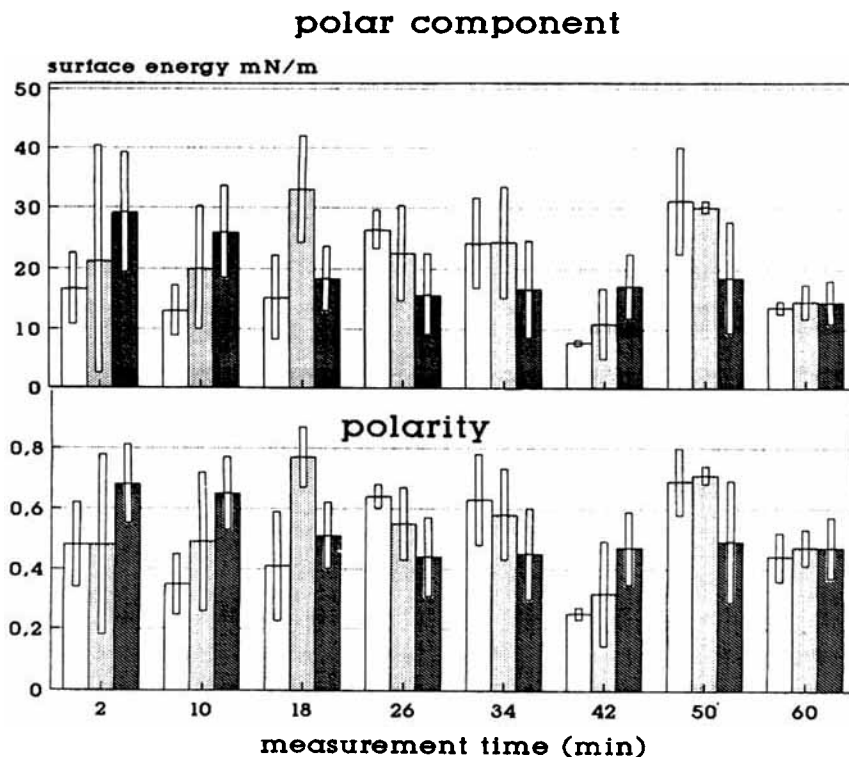


Figure 2 Air plasma treatment of polypropylene surfaces, using a 120 s plasma exposure time. Symbols are the same as in Figure 1.

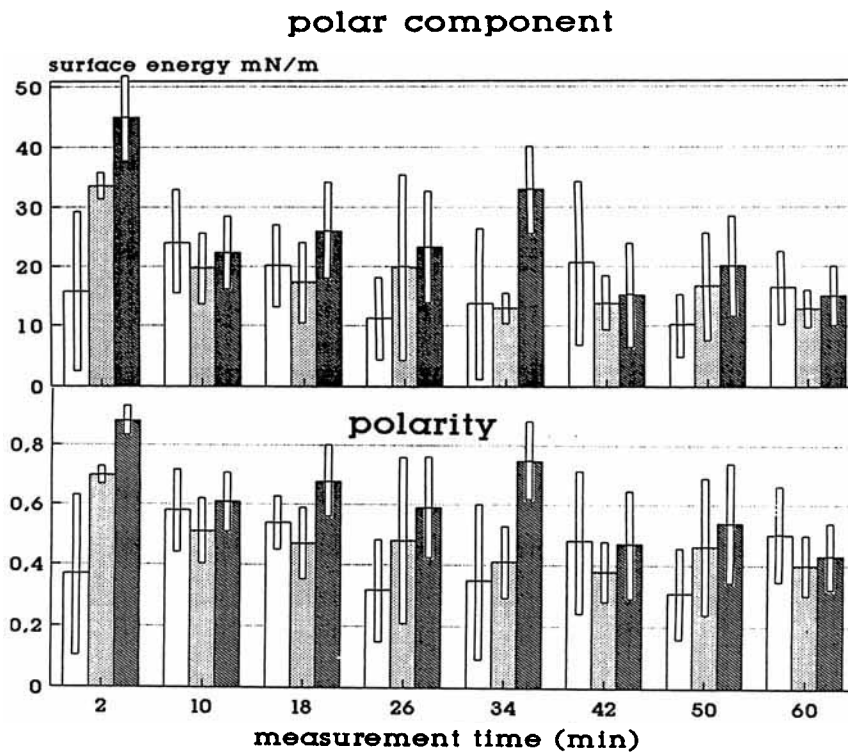


Figure 3 Air plasma treatment of polypropylene surfaces, using a 150 s plasma exposure time. Symbols are the same as in Figure 1.

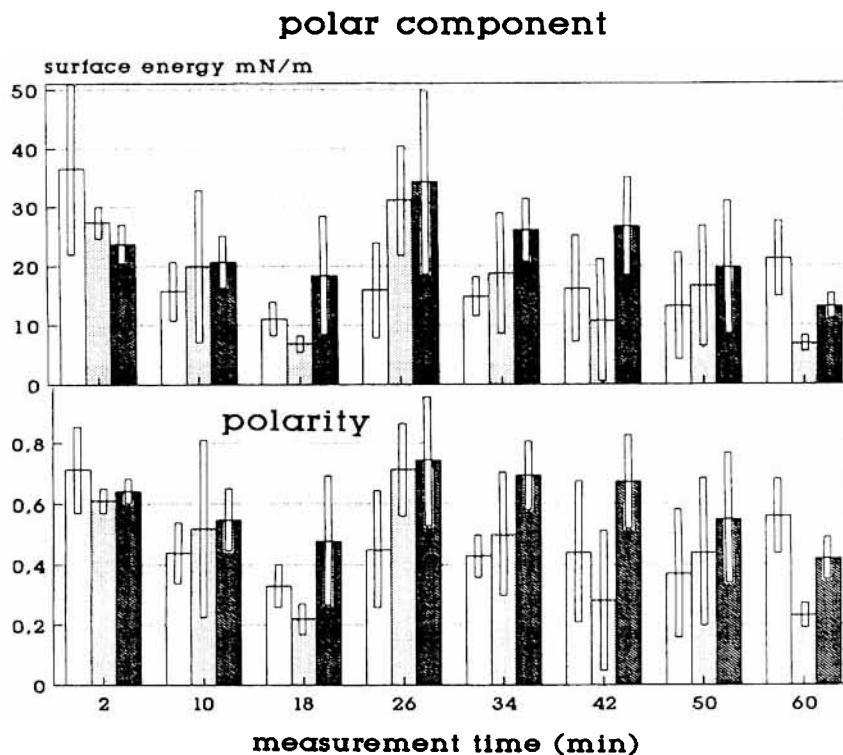


Figure 4 Air plasma treatment of polypropylene surfaces, using a 180 s plasma exposure time. Symbols are the same as in Figure 1.

No clear trends as a function of measurement time can be distinguished.

A.2. Changes Occurring between 1 and 4 H after Treatment

The trends observed in the 2–60 min measurement time interval are continued in the time range from 60 to 240 min. The 90 s treatment (Fig. 5) gives rise to somewhat lower polarity values (≈ 0.4), as compared to Figure 1 (≈ 0.5). The standard deviations are mostly similar throughout the series of measurements presented in Figure 5. An extension of the treatment to 120 s (Fig. 6) results in a more uniform time dependence over the period of observation; note, in particular, the stability of the values obtained for the polar component of the surface energy for treatment in dry technical air. The standard deviations are reduced, as compared to the 90 s treatments; the large excursions seen in Figure 5 are apparently absent in Figure 6.

With 150 s of treatment time in moistured technical air (Fig. 7), the behavior of the averages in the measurement time from 1 to 4 h is not quite as uniform as observed after 120 s treatments; also, the standard deviations in Figure 7 are somewhat larger than those determined for the data in Figure 6.

Large excursions of the average values and large standard deviations observed after 180 s of treatment (Fig. 8) indicate that the surfaces have been overtreated: The resulting state of the surface is nonuniform and subject to large variations between the measurements.

B. Surface State after Plasma Exposure followed by Posttreatment

The aim of this second part was to investigate whether the surface properties of the plasma-treated polypropylene plaques can be improved by a simple posttreatment procedure, i.e., by immersion into water subsequent to plasma exposure. This method is motivated by the concept that unstable functional groups introduced on the surface in the air plasma, such as hydroperoxides, might be converted into more stable chemical forms in the aqueous reaction medium. Immediately after the plasma exposure, the plaques were immersed into water, under the conditions specified below.

B.1. Plasma Treatment in Dry Technical Air for 120 s

B.1.1. Posttreatment in Hot Water (95°C).

After ending the plasma treatment, the plaques were immediately immersed into hot water. The solution

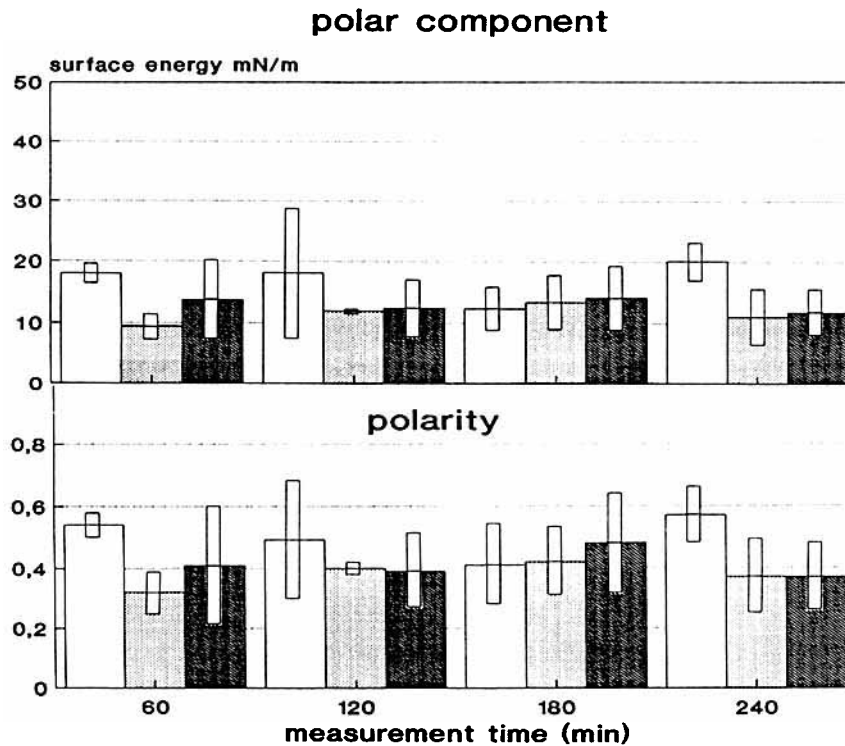


Figure 5 Air plasma treatment of polypropylene surfaces, using a 90 s plasma exposure time. The measurements of Figure 1 are continued over the interval from 60 to 240 min after plasma exposure.

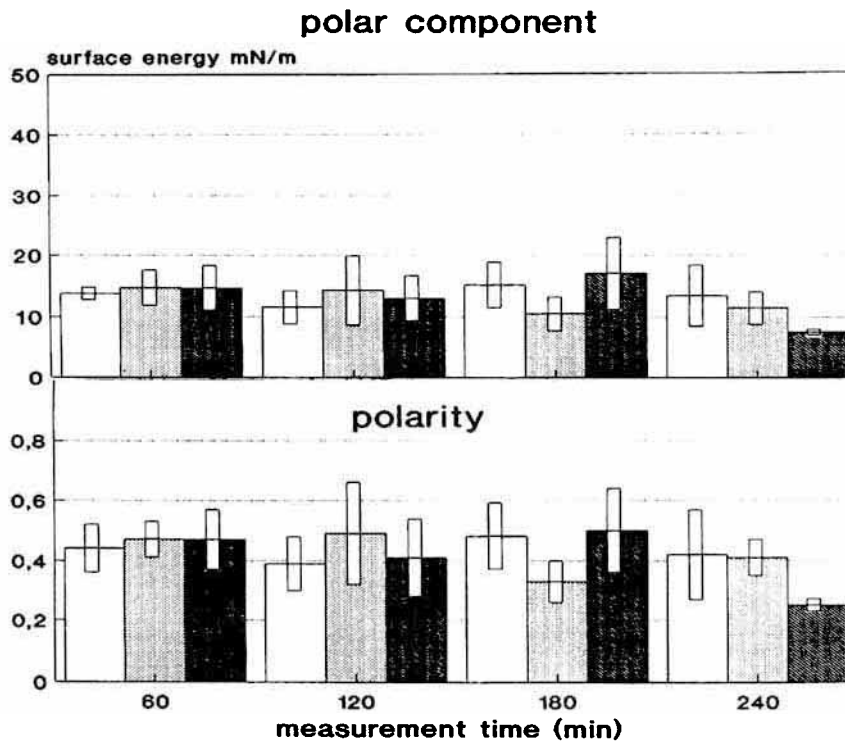


Figure 6 Air plasma treatment of polypropylene surfaces, using a 120 s plasma exposure time. The measurements of Figure 2 are continued over the interval from 60 to 240 min after plasma exposure.

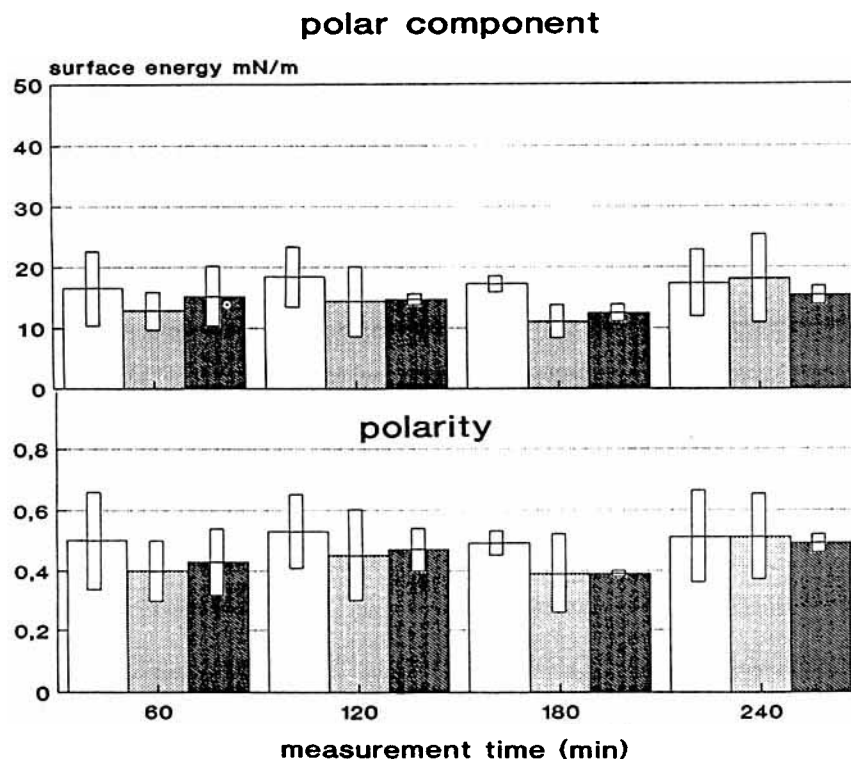


Figure 7 Air plasma treatment of polypropylene surfaces, using a 150 s plasma exposure time. The measurements of Figure 3 are continued over the interval from 60 to 240 min after plasma exposure.

was stirred by moving of the plates. A short (2 min) and a long (30 min) immersion time have been tested. After the exposure to water, the plaques were dried at 85°C for 30 min and brought to room temperature in a desiccator during a time of 30 min.

Surprisingly, both treatments seemed to reverse the effects of the plasma treatment, as judged from the measured values of the surface energy. The surface tension does not change within 1 h after the described procedure. This is shown by the values measured after 0, 30, and 60 min, as collected in Table I.

B.1.2. Posttreatment in Distilled Water at Room Temperature. The plasma treatment and the immersion procedure were the same as described in the preceding section. A drying time of 15 min at 85°C and an equilibration time of 15 min in the desiccator were used. These times were found to be necessary for obtaining a dry polypropylene surface, on which meaningful contact-angle measurements can be performed. The results are summarized in Table II and Figure 9.

After 2 min of immersion in water at room temperature, the polar component of the surface en-

ergy (Table II) rises to a value three times higher than the one found after immersion in hot water. The polarity rises from a value of 0.07 (hot water treatment) to a value of 0.34 ± 0.07 . The total surface energy remains remarkably constant at 28.0 ± 4.1 mN/m.

As mentioned above, the solution containing the immersed plates was stirred for this set of measurements. However, stirring was found to scratch the surfaces of the plaques; these scratches severely impede the following contact-angle measurements. To exclude the perturbations of the surface energy determinations resulting from stirring, another series of measurements was made in such a manner that the plasma-treated surface was just immersed into water, without stirring. The treated surface was brought into contact with water first. The contact-angle measurements were subsequently performed on this side. The latter procedure, i.e., contacting the plasma-treated side with water without stirring, was used in all the experiments reported below. The drying time was 15 min and the equilibration time in the desiccator, also 15 min. After this treatment, the surface energies of the corresponding set of sample plaques were measured sequentially.

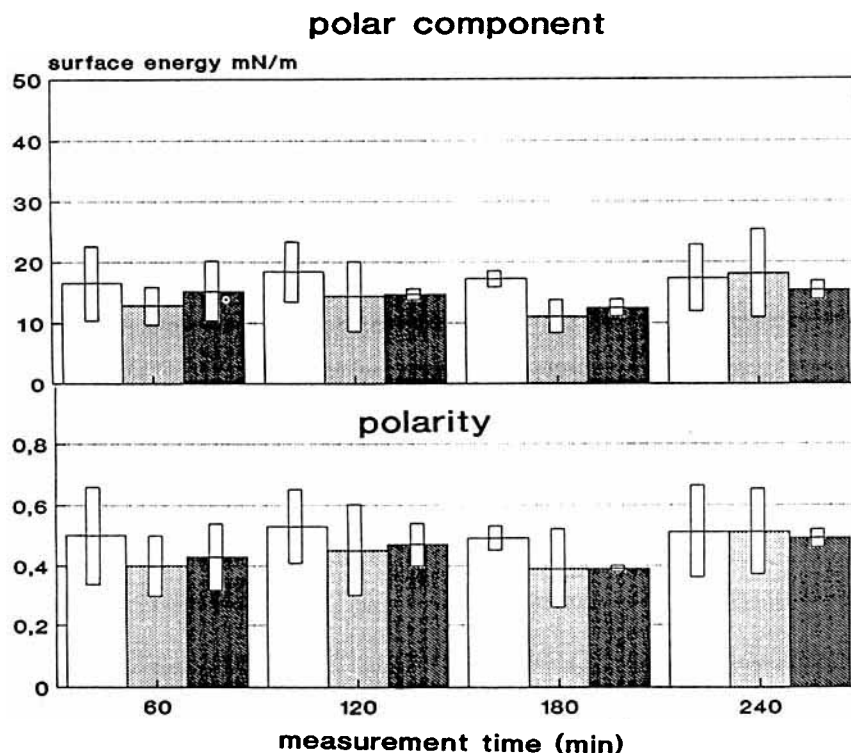


Figure 8 Air plasma treatment of polypropylene surfaces, using a 180 s plasma exposure time. The measurements of Figure 4 are continued over the interval from 60 to 240 min after plasma exposure.

In the absence of stirring, a residence time in water between 2 and 5 min (Table II; Fig. 9) brings the polar component of the surface energy up to values of 10–13 mN/m. The corresponding polarity values are found to vary between 0.34 and 0.49. A further increase in the immersion time to 10 min results in polar components ranging from 9.6 to 26.5

mN/m (average 16.5 mN/m), with a very large scatter.

B.1.3. Posttreatment in Distilled Water at Room Temperature followed by Cold Air Drying. A further measurement was made with 2 min of immersion in water at room temperature.

Table I Surface Energies^a Measured after Immersion in Water at 95°C

Time of Measurement	Polar Component	Dispersive Component	Total Energy	Polarity
<u>2 min immersion</u>				
0 min	1.60	23.3	25.0	0.064
10 min	1.90	23.1	25.0	0.076
Average	1.75 ± 0.2	23.2 ± 0.14	25.0	0.070 ± 0.008
<u>30 min immersion</u>				
0 min	1.5	29.4	31.0	0.048
30 min	4.8	23.5	28.3	0.170
60 min	1.9	31.2	33.1	0.057
Average	2.7 ± 1.8	28.0 ± 4.0	30.8 ± 2.4	0.092 ± 0.07

^a All surface energies are given in mN/m.

Table II Surface Energies Measured after Immersion in Water at Room Temperature (25°C)

Treatment	Polar Component	Dispersive Component	Total Energy	Polarity
2 min, with stirring	7.5 ± 3.0	20.5 ± 5.3	28.0 ± 4.1	0.34 ± 0.07
2 min, without stirring	12.8 ± 3.6	13.2 ± 3.7	26.1 ± 0.9	0.49 ± 0.14
5 min, without stirring	10.3 ± 1.6	20.4 ± 4.6	30.7 ± 4.1	0.34 ± 0.07
10 min, without stirring	16.5 ± 8.9	18.7 ± 8.2	35.2 ± 3.0	0.46 ± 0.23
2 min, cold air drying	16.5 ± 4.4	17.6 ± 3.5	34.1 ± 2.6	0.48 ± 0.11

Subsequent to the water treatment, the plaques were dried for 10 min with a cold air fan and equilibrated for 15 min in the desiccator. The polar component thereby obtained (Table II; Fig. 9) is higher than found with the previously reported treatments. At the same time, the standard deviation rises, as compared to the aforementioned measurements. This is due to a problem arising from the drying technique: Large quantities of *dust particles* are blown onto the plaque by the fan, which makes the contact-angle measurements difficult. The polarity and its standard deviation are comparable to those reported above for 2 min of posttreatment in water at 25°C.

B.1.4. Posttreatment in Cold Water (3°C). Standard drying times were used as described in the Experimental section. Surface energy data obtained are presented in Table III. The results for the polar component are also too nonuniform such that this type of treatment was not further pursued.

B.1.5. Reference Measurements without Water Immersion. After the plasma treatment (120 s, dry air), the plaques were dried for 15 min at 85°C and equilibrated for 15 min in the desiccator. Then, the surface energy was measured in intervals of 15 min. The results presented in Table IV show

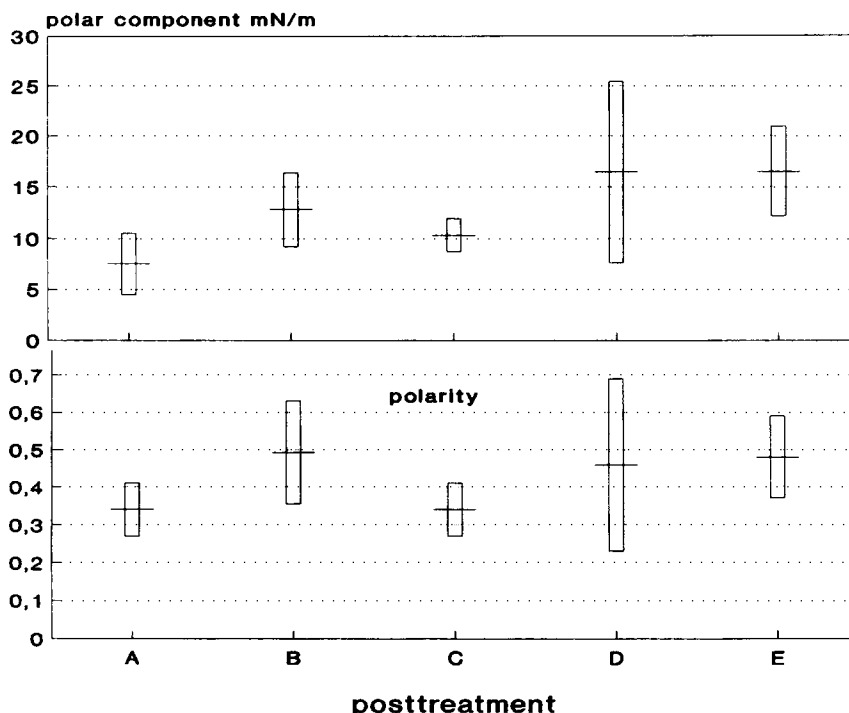


Figure 9 Posttreatment of polypropylene plaques in water at room temperature, subsequent to 120 s of plasma exposure in dry technical air: (A) 2 min of immersion with stirring; (B) 2 min of immersion without stirring; (C) 5 min of immersion without stirring; (D) 10 min of immersion without stirring; (E) 2 min of immersion without stirring, followed by cold air drying with a fan.

Table III Surface Energies Measured after Immersion in Cold Water (3°C)

Treatment	Polar Component	Dispersive Component	Total Energy	Polarity
2 min immersion	16.4 ± 5.2	17.4 ± 0.9	33.9 ± 4.9	0.477 ± 0.094
5 min immersion	15.0 ± 9.5	19.1 ± 4.4	34.1 ± 5.2	0.418 ± 0.208

values that are not too different from those obtained for the plates immersed in water (cf. Table II). We tend to attribute this behavior to the natural humidity of the air contained in the drying oven.

B.2. Plasma Treatment in Moistured Technical Air for 120 s

In view of the results obtained in the preceding section, the plasma-treated plaques were subject to the drying/equilibration procedure without immersion into water. It was assumed that the plaques had received sufficient exposure to humidity during the plasma treatment in moistured technical air. The drying time in the oven at 85°C and the equilibration time in the desiccator at room temperature were varied.

In the first set of experiments, the drying and equilibration times were both set to 15 min, i.e., chosen identical to the standard procedure reported in Section B.1.2. Results are presented in Table V; a polarity value of 0.38 was determined. Surface energies obtained upon increasing the drying time to 30 min indicate (Table V) that this residence time at 85°C is too long for the selected plasma treatment. The standard deviation obtained for the polar component is twice as large as the one obtained with the more gentle treatment of 15 min drying.

Similar observations are made if the time in the desiccator is doubled to 30 min. The results, included

in Table V, are too nonuniform to be pursued any further (cf. the standard deviation of the polar component).

In summary, plasma exposure in moistured technical air followed by heat treatment at 85°C showed no advantages as compared to the procedures reported in Section B.1. It thus appears preferable to immerse the plaques into room-temperature water after plasma treatment in dry air. This immersion creates better-defined conditions for the reaction of unstable surface functional groups, as compared to the exposure to water vapor during plasma treatment and drying.

DISCUSSION

A. Influence of Plasma Treatment Time

In all cases, the plasma treatment leads to an increase of the polar component of the surface energy of polypropylene. However, the various types of air medium employed result in a different quality of the surface treatment. With dry air and short plasma exposures, a minimum in surface energy is observed ≈ 40 min after the treatment. The absence of this minimum appears to be a useful criterion to establish a lower bound for the length of the plasma treatment required to achieve adequate surface modification.

In a large series of additional experiments, a min-

Table IV Surface Energies Measured in the Reference Experiment without Water Immersion

Time	Polar Component	Dispersive Component	Total Energy	Polarity
Sample 1				
0 min	8.8	8.0	26.8	0.328
15 min	8.9	18.3	27.1	0.328
30 min	6.8	21.7	28.6	0.237
Sample 2				
0 min	5.5	19.4	25.0	0.220
15 min	9.8	21.1	30.9	0.317
30 min	14.0	24.6	38.5	0.364
Overall average	9.0 ± 2.9	20.5 ± 2.5	29.5 ± 4.8	0.300 ± 0.06

Table V Surface Energies of Plaques after Plasma Treatment in Moistured Technical Air followed by Posttreatment

Treatment	Polar Component	Dispersive Component	Total Energy	Polarity
Drying time of 15 min, equilibrium time of 15 min	11.0 ± 4.2	17.3 ± 3.3	28.3 ± 3.2	0.38 ± 0.12
Drying time of 30 min, equilibrium time of 15 min	17.8 ± 9.1	14.2 ± 3.5	32.0 ± 6.3	0.53 ± 0.18
Drying time of 15 min, equilibrium time of 30 min	16.4 ± 11.0	17.4 ± 5.5	33.8 ± 6.0	0.45 ± 0.25

imum in surface energy was reproducibly observed after ≈ 40 min if treatment times were insufficient. Within the data set presented above, this minimum in surface energy is most clearly seen for a treatment time of 90 s in dry media (Fig. 1). For 120 s of treatment time (Fig. 2), the times of occurrence of surface energy minima differ slightly between the reaction media employed. If the treatment time is raised to 150 s, the minimum at ≈ 40 min is no longer observed.

Overlooking all series of data, the averages of the polar component of surface energy are in the range between 10 and 30 mN/m. The averages after 90 s of treatment exhibit large statistical fluctuations. Plasma treatment of 120 s results in a much more reproducible and less stochastic behavior. With longer treatment times, the fluctuations become larger again. Extraordinarily high values of the polar component observed after 150 s of treatment (data taken 2 min after treatment, Fig. 3) point to the fact that the surface of the system is far from equilibrium.

If the plaques are stored for longer times after the plasma treatment, the surface energy results become more uniform again. This indicates that the systems are approaching a stable equilibrium situation.

A.1. Changes Occurring within 60 Min after Treatment

It has been established that an appropriate balance of polar and dispersive components is desired for a reliable adhesion of, e.g., paints on polypropylene surfaces. The aim of the plasma treatment performed in this study is therefore to achieve polar and dispersive components of equal size, which corresponds to a polarity (polar component divided by total surface energy) of ≈ 0.5 .

In comparison with other techniques, plasma treatment may lead to comparatively constant and

reproducible values of the surface energy. The present data show a pronounced dependence on the reaction medium used and on the treatment time.

The requirement of 50% polarity is fulfilled best when using moistured technical air and a treatment time of 120 s (Fig. 2). Stable values of the averages are approached within ≈ 20 min after plasma treatment. The state of the surface reached after this time does not change significantly any more for the next 60 min. The experimental standard deviations are fairly constant over the mentioned interval. As the total surface energy is found to be essentially constant over the period of observation, the behavior of the polar component and of the polarity (Fig. 2) mirror each other.

A tentative explanation for this behavior on a molecular level has to consider the secondary reactions of hydroperoxide and radical functional groups generated by the plasma treatment. It is suggested that a reaction time of ≈ 20 min in a saturated water atmosphere is sufficient for the surface reactions to reach a stable (or metastable) state that does not change significantly any more during the subsequent period of observation.

By ranking the results with respect to the aims of 50% polarity, constancy of the polar component, and high reproducibility, the treatment in *dry technical air* for 150 s (Fig. 3) appears close in quality to the one discussed above (*moistured technical air*, 120 s, Fig. 2), although the constancy of the values is not as satisfactory.

Treatment times that are likely not to be of practical use (for the given plasma parameters) are plasma exposures in technical air for either 90 or 180 s. As referenced to the treatment identified above as the best one (120 s of exposure in moistured technical air), 90 s of treatment time is not sufficient with the dry gases. This may be judged from the pronounced decrease of the polar component after ≈ 40 min (Fig. 1). This minimum in the polar component shows up with dry reaction media up to a

treatment time of 120 s. For longer treatment times, the minimum is not further observed, as mentioned above.

The observed minimum in surface energy is associated with rotations (i.e., torsional motions) of the polymer chains. With insufficient treatment, the macroscopic surface energy returns to a value similar to the one of the untreated surfaces after a time of ≈ 40 min. This is the only minimum observed in the monitored time interval after treatment. Some 10–20 min later, the polarity returns to values that are typical for a plasma-treated surface. It appears that the hydroperoxide groups, which are initially created by the plasma treatment, have a tendency to reorient toward the interior of the polymer. This conformational change is overlaid by secondary reactions of the hydroperoxide groups, which eventually restore (potentially different) polar functional groups on the surface and result in the observed long-time values for the polar component of the surface energy.

It is interesting to compare the treatments in moistured technical air (120 s) and in dry air (180 s). The starting value of the polar component is much higher with the dry air plasma (180 s)-treated plaques. However, after ≈ 25 min, comparable values are obtained as in the case of the moistured technical air. An intermediate minimum in the polar component of the surface energy, which is observed ≈ 20 min after the dry-air treatment, is less pronounced with the plaques treated in moistured technical air. Apparently, a rigorous treatment (for 180 s) in dry air leads to a faster approach to the equilibrium state, as compared to the shorter treatment (120 s) in the same medium.

A.2. Observations in the Interval of 60–240 Min after Treatment

The trends discussed above for the first hour of measurement after treatment are observed to continue. Plasma treatments longer than 120 s are disadvantageous: They result in large irregularities on the surface, as evidenced by strong fluctuations in the polarity. Standard deviations are higher than ± 0.1 ; for a polarity of ≈ 0.4 , this corresponds to relative standard deviations of $\approx 25\%$. Fluctuations become even larger if the plasma treatment time is raised up to 180 s (standard deviations of the polarity ± 0.12 or larger, relative standard deviations exceeding 30%).

Treatment in dry technical air dry for 120 s excels in this time interval of observation, by a high constancy in the values of the polar component and of

the polarity. The values of the polar component range between 13 and 15 mN/m, which corresponds to a polarity of ≈ 0.4 .

Slightly inferior to this treatment are the results of a 150 s plasma exposure in moistured technical air. The fluctuations in the polar component and polarity are somewhat more pronounced than in the aforementioned treatment.

Treatment times of 90 and 180 s will not be considered in further experiments because of the unsatisfactory results obtained. Both treatments yield inadequate surface treatment and large fluctuations. Ninety seconds of treatment seem to be insufficient and 180 s to be too long for the desired surface modification of SP 179 plaques.

B. Influence of Posttreatment

The most significant results are summarized in Figure 9 and in Tables II and III, which will now be discussed. Results from the immersion in water at room temperature subsequent to a 120 s plasma treatment in *dry air* are presented in Figure 9. After 2 min of immersion (with stirring), a polar component of the surface energy of 7 mN/m is obtained. Increasing the immersion time to 5 min results in an increase in the polar component to 10 mN/m, with a small standard deviation. Longer immersion times give rise to even higher values of the surface energy, but the associated variance in the data largely increases as well.

It appears not to be important whether the plaque is dried in cold or warm air, as may be judged both from the polar component of the surface energy and from the associated polarity values (Fig. 9). Drying with cold air results in a smaller standard deviation of the polarity.

The use of moistured technical air, combined with drying in an oven at 85°C, results in values of the polar component of ≈ 11 mN/m (Table V). A polarity of ≈ 0.4 , associated with a small standard deviation, is reached when a value of 15 min is chosen both for the drying time and the subsequent equilibration time. Both an extension of the drying time to 30 min or an extension of the equilibration time, result in a significant increase in the standard deviations. The values of the polarity obtained with the latter two procedures are close to the desired value of ≈ 0.5 , but the fluctuations determined for the polarity are even more pronounced. This behavior is interpreted as follows: A nonuniform treatment of the surface gives rise to patches characterized by different surface properties. Surface-tension measurements on such an inhomogeneous

surface are subject to large fluctuations. Thus, the observation of a large standard deviation may taken as an indication that the particular treatment does not result in uniform values of the surface tension, as desired for reliable adhesion of coatings.

Functional groups introduced on the surface of polypropylene during the plasma treatment are known to possess considerable mobility. A rotation of hydroperoxide groups into the inside of polypropylene has been proposed.¹¹ The driving force for the rotation of hydroperoxide groups from the surface into the bulk of polypropylene is the tendency to achieve a thermodynamic minimum of the surface free energy. This notion is consistent with our results obtained with posttreatment of the plasma-exposed parts, in particular, by the immersion in hot water. The heating of the surface to 95°C provides the activation energy that is necessary for the rotation of the chains. After the hydroperoxide groups have been reoriented toward the interior, they cannot react any further with water on the surface. Therefore, the surface shows an unpolar character after the immersion treatment.

These findings are not in agreement with a recent publication of Occhiello et al.,¹¹ where it was stated that a significant concentration of polar groups resides on the surface of polypropylene even after heating. A likely cause for the discrepancy lies in the fact that the conclusions of Occhiello et al. have been based on the contact angle measured using a single liquid. Our experience shows that, at least, a second liquid must be monitored, preferably a fluid for which the contact angle varies over a wide range on the surfaces investigated.

The posttreatment in water cooled to 3°C (Table III) yields the least satisfactory results. Immersion for 2 min produces a polar component of the surface energy of 17 mN/m; 5 min of treatment leaves the average essentially unchanged, but result in a twice as large standard deviation.

CONCLUSIONS

From the results of the present investigation, the following guidelines can be deduced for the plasma treatment of polypropylene surfaces (in particular, the SP 179 formulation). If rapid processing of the plasma-treated parts is desired, the reactive medium should be saturated with moisture during the plasma treatment. On the other hand, if sufficient time is provided for the surface to reach an equilibrium state, dry gases can be used for the treatment.

A treatment time of 120 s, for the given plasma

parameters, results in a reproducible surface state exhibiting the desired values for the polar part of the surface energy and the polarity. The somewhat longer treatment of 150 s yields results that are only slightly inferior to the 120 s exposure.

Immersion of the plasma-treated plaques into aqueous media at 95°C was found to deteriorate the quality of treatment, as the polarity values are observed to decrease. This behavior has been interpreted in terms of a reorientation of the polar groups created, toward the interior of the polymer. In contrast, upon water immersion at room temperature, the described change in conformation is much slower; therefore, a reaction of the hydroperoxide groups with water resulting in chemically stable functional groups does occur, as shown by the large values obtained for the polar component of the surface energy.

Whereas oxygen plasmas have been preferentially used in previous investigations,^{7,9,11,12} the present plasma treatments have been performed in an air plasma. In air, not only oxygenated species are generated: From a study of corona treatment of polypropylene in nitrogen and carbon dioxide,¹⁴ it has been shown that tertiary radicals situated on carbon are generated by activated nitrogen. As these species are unlikely to be completely shielded by rotation into the bulk, the reaction of these radical sites with water might constitute an important contribution to the high-polarity values obtained after immersion into water at room temperature. The latter contribution would be absent on the surfaces investigated by Occhiello et al.,¹¹ which had been treated in a pure oxygen plasma. The surface-energy measurements show that an efficient posttreatment is achieved by immersion into water at room temperature, using exposure times no longer than 5 min.

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