Pretreatment of Polypropylene Films for Following Technological Processes, Part 2: The Use of Low Temperature Plasma Method

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ABSTRACT: The surface of polypropylene (PP) films was activated by RF plasma method with the use different gases: argon, air, water vapor, and acetic acid vapor. Plasma was diagnosed based on spectra emitted by gas plasma using the method of optical emission spectroscopy. The effectiveness of these processing gases during plasma treatment was analyzed. The effects of PP activation were assessed with the use of IR-ATR absorption spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy, and the analysis of the surface free energy components based on liquid contact angle. The activation of PP surface by plasma treatment resulted in the increased energy of PP surface layer to the extent being dependent on the type of processing gases and in the formation of new chemical groups on it. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2529–2541, 2011

Key words: poly(propylene); films; low temperature plasma treatment

INTRODUCTION

A distinctive feature of polypropylene (PP) products is their low free energy of surface.[1,2] This property is desirable and exploited wherever such a product is to be chemically and physicochemically inert in relation to the other phase, showing, for instance, oleophobic or hydrophobic properties. However, in PP processing concerning the surface of product such as sizing, grafting, printing, metalizing, depositing thin functional organic, or inorganic layers, the PP surface is required to show the highest possible level of free energy. The free energy of a polymeric substrate surface, often identified with surface tension,[3] should be at least equal to the surface energy (surface tension) of the glues, resins, printing pastes, or deposits applied. Such a relation of surface energies provides a strong molecular interaction between the surface of PP substrate and the material deposited (glue, printing paste, thin layer, etc.).

To fulfill the above condition, the PP surface is activated prior to the technological operations mentioned above. The comparative analysis of the activation of PP substrates by conventional chemical methods, electrochemical method and UV irradiation is presented in Part I of this study.[4] The present Part II includes the activation of PP by means of low-temperature RF plasma. This pro-ecological and operator-friendly technique is used wherever the use of conventional chemical processes is limited or impossible. The processes proceeding in plasma are dry, with the use of an extremely low consumption of chemicals and water, without harmful and toxic by-products. The plasma of a process gas interacts with the surface layer of polymeric substrate and does not affect the polymer in volume. The effects of plasma on the surface layer of polymers, reported in papers [5–8] indicate that there occur elementary processes such as functionalization, crosslinking, degradation, and material etching in the polymer surface layer at the same time. To select a specified elementary process as the dominating reaction, for example, the functionalization of the surface layer, one has to fulfill appropriate technical conditions for this process: the composition of process gas, excitation conditions including frequency, applied effective power, gas pressure and flow rate, as well as the location of substrate in a reactor, etc.[9] The functionalization of PP surface is performed with the use of chlorine compound plasma including: carbon tetrachloride, chloroform,[10,11] 1,2-dichloroethane[10] as well as argon,[12] oxygen,[13] nitrogen,[14,15] carbon dioxide,[8] and air plasma.[16–18] Generally, these types of plasma are capable of increasing the wettability, free surface energy and adhesive strength of the polymer surface layer. Oxygen plasma is considered one of

the most active ones. The interaction of molecules of this plasma results in the formation of various oxygen groups in the polymer surface layer: C—O, C=O, O—C=O, C—O—O, etc. The processes of oxidation proceed intensively to release polymer degradation products (etching). The nitrogen plasma treatment results in increased content of nitrogen in the form of groups such as C—H, C—NH—C, C=N, NH$_2$[19] as well as oxygen groups after a longer plasma treatment. Consequently, high adhesion stability is obtained. Air plasma oxidizes the polymer treated and the effect obtained is of synergic character depending on the composition of air. Mostly CO groups are formed in the surface layer of polymer. The chlorine compounds plasma implants chlorine into the PP structure and the effects obtained are the same as those in the case of oxidation. The analysis of the plasma treatment of PP substrates is aided by plasma diagnosis by means of which one can identified the course of elementary processes in plasma.[20,21]

The aim of this study was to activate (oxidize) the surface of PP and to make the diagnosis of the state of process gas plasma, using three gases: air, water vapor, and acetic acid vapor, and additionally an inert gas: argon for comparison purposes. Plasma was diagnosed based on spectra emitted by gas plasma using the method of optical emission spectroscopy (OES). The effects of plasma treatment on PP were assessed by means of the IR-ATR absorption spectroscopy and scanning electron microscopy (SEM), while the components of the surface free energy were analyzed by testing the sessile drop wettability and adhesion properties by the Peel Test method. Two types of PP film with various physical microstructures were used: (a) noncrystalline and nonoriented film and (b) crystalline and two-direction-oriented film.

There were established technical conditions of PP treatment with RF plasma, under which etching processes are limited, new functional groups are formed on the polymer surface and the surface free energy is increased. The ageing of PP modified with plasma was also examined.

EXPERIMENTAL

Materials

Two types of commercial transparent PP films with no anti-photooxidation additives (Petrochemia P[swsl]lock S.A) were used in the investigations: (1) a nonoriented CAST PP film with a nominal thickness of 30 μm, (softening point: 152°C, birefringence coefficients: $\Delta n_\alpha = 0$, $\Delta n_\beta = 0$), (2) a bidirectionally oriented PP AG film (BIFOL), with no weldable layers, with a nominal thickness of 30 μm, a density of 0.91 g/cm^3 (softening point 166°C $\Delta n_\alpha = 0.151$;

$\Delta n_\beta = -0.0145$). The PP AG films are characterized by a crystalline degree of 45%. The pretreatment processes were carried out using PP samples preliminarily purified by extraction with methanol.

The following gases were used in the study: argon 99,995 (Air Liquide), air 99,995 (Air Liquide), and also the following liquids: analytically pure (a.p.) methylene iodide (Fluka Chemika), distilled water, (a.p.) and acetic acid (POCh S.A., Poland).

Plasma treatment of PP films

PP films were treated by electrode-less plasma discharge, capacitive type, induced by means of RF field of 13.56 MHz. The RF generator used (coupled to the reactor tube by means of external capacitor plates through a matching network) made it possible to control power within the range 10–300 W.

The glass reactor tube (diameter: 9 cm, length: 50 cm) was evacuated by a two-stage rotary pump. A micrometer leak valve and mass flow controller (MKS Instruments) controlled the process gas flowing along the axis of the tube. The pressure of gases was monitored by a resistance gauge within the range 10^{-3}–1 Tr. PP film samples were placed in the reactor along its central axis on a glass carrier.

Atomic and molecular plasma species were analyzed with the use of a High-Resolution Spectrometer, type HR 2000 from Ocean Optics, equipped with the software. The spectrum of plasma gas was recorded through a quartz window placed centrally in the reactor axis, by means of an optical waveguide detector within the wavelength range from 280 to 630 nm (integration time: 50 ms). The plasma discharge was induced in argon, air, water vapor, or acetic acid vapor. The spectra emitted by the process gas plasma induced under various gas pressures and with various power values generated were recorded. The identification of the atomic and molecular plasma species was carried out on the basis of data base.[22] and the articles[23–30]

Test methods

Examination of the chemical structure of PP surface by means of IR-ATR absorption spectroscopy

The IR spectrophotometric examination of PP film surface was performed by the ATR-IR technique using an attachment with KRS-5 crystal and a FTIR-8300 spectrophotometer. IR spectra were recorded as a function of transmitance within the range of wave numbers from 400 to 4000 cm^{-1}.

X-ray photoelectron spectroscopy (XPS)

XPS measurements were carried out on a XPS spectrometer with a double cylindrical mirror analyzer

(Physical Electronics) and X-ray gun (VSW, UK). The core-level signals were obtained at a photoelectron take off-angle of 45° with respect to the sample surface. Surface elemental stoichiometries (% Atomic Concentration) were determined from peak-area ratios after correcting with the experimentally determined sensitivity factors. All the binding energies were referenced to the C 1s peak for adventitious carbon at 284.6 eV. The identification was carried out on the basis of data base for polymers[31] and the article[32]

Examination of PP film surface by atomic force microscopy (AFM)

AFM measurements were carried out to observe surface topography of the samples before and after plasma treatment. The AFM used was a MultiView 1000 from Nanonics Imaging operated in tapping mode. There was used a gold-coated glass blade from Nanonics, type SuperSensor[TM], with a curvature radius $\phi = 10$ nm and frequency 40 kHz. The scanning area for all samples: 5000×5000 nm^2. The analysis of results was performed by means of program WSxM 5.0[33]

Testing the changes in the free energy of PP film surface

The surface tension of PP film as equivalent of the free energy of surface was determined on the basis of advancing angle "Θ"; of the liquid deposited on the film surface. There were used test liquids with specified components of surface tension: dispersive component "γ_d" and polar component "γ_p." The liquids used included: distilled water as polar liquid ($\gamma_d = 21.8$ mJ/m^2, $\gamma_p = 51.0$ mJ/m^2) and methylene iodide as dispersive liquid ($\gamma_d = 49.5$ mJ/m^2, $\gamma_p = 1.3$ mJ/m^2). The advancing angle was tested by the sessile drop method.[34] The free energy components of PP surface: dispersive γ_d^f and polar γ_p^f were calculated according to Owens-Wendt's procedure.[35]

The peel test

The adhesion test was performed using Instron Tensile Tester TMM 1111. Bonding strength was measured by the T-Peel method. A commercial Tesa adhesive tape from Sparta (Michigan/USA) was stuck to the PP film surface freshly treated by plasma discharge. After 10 days the bonding strength between the tape and PP film surface was measured at a peeling angle of 180° and a peeling rate of 1 cm/min. Prior to measurements, the samples were conditioned in air ($t = 20$°C, RH = 65%).
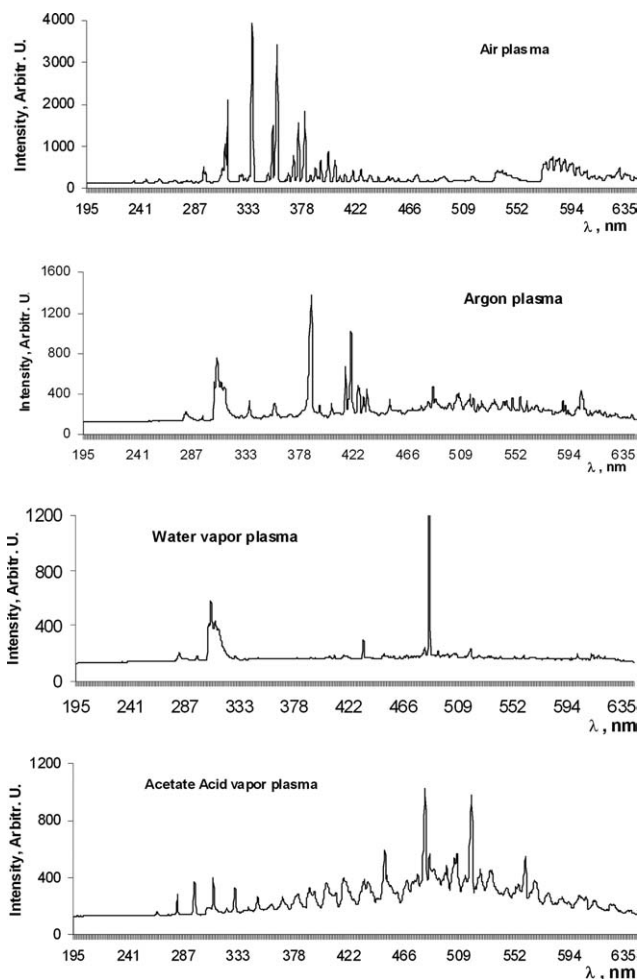

Figure 1 Optical emission spectra of processing gases in plasma state (0.1 Tr, 100 W, and 3 sccm).

RESULTS AND DISCUSSION

Characteristics of RF plasma of process gases in capacitive type plasma

Gas plasma in glow discharge is formed by chemical species such as nonionized molecules, atom radicals, molecular radicals, electrons, ions, etc. The susceptibility to induction and ionization as well as the processes of recombination of chemical species are characteristic of the given type of gas.[36,37]

The elementary processes taking place in plasma are accompanied by the emission of electromagnetic radiation within the range of visible and ultraviolet light. Figure 1 shows emission spectrograms recorded within the range 280–630 nm for argon, air, water vapor, and acetic acid vapor plasma induced with a power of 100 W under a pressure of 0.1 Tr. These spectrograms indicate the occurrence of two types of radiation: continuous (emitted with the inhibition of free electrons in plasma) and linear radiation (emitted with electrons passing between discrete levels of energy in atoms, molecules, and ions). The linear radiation carries information about plasma
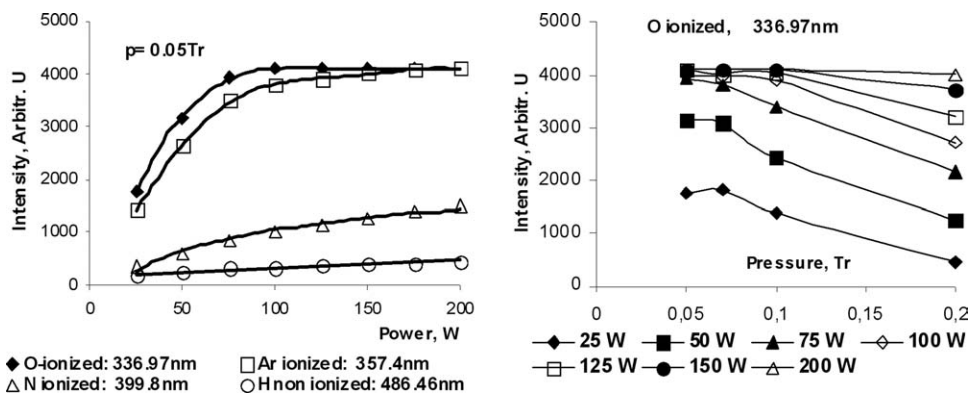
Figure 2 Optical emission spectrum of air plasma species as a function of power and pressure.

parameters: composition, concentration and temperature of electrons, and chemical species.[38] The intensity of the spectral line of a specified plasma chemical species depends directly on concentration.[38] In this study, the identification of species was limited to the use of spectral lines and a comparative analysis of intensity of these lines, while the spectra were not calibrated.[36]

The emission spectrograms in this study were recorded under various gas pressures in glow discharge (0.02–0.2 Tr) and flowing (0.2–20 sccm) using various values of the effective power supplied to the reactor (25–300 W). The effect of pressure and effective induction power on the character of spectra and the emission lines intensity of species was analyzed (Figs. 2–5).

Air plasma

The spectrograms recorded for air plasma within the power range from 25 to 200 W under pressures from 0.05 to 0.20 Tr indicate the occurrence of characteristic spectral lines generated by the components of air: oxygen, nitrogen, argon, and hydrogen. The changes in discharge parameters were accompanied by changes in the spectral line intensity and new lines

were not formed. The spectral line intensities of oxygen (336.97 nm), argon (357.4 nm), nitrogen (399.8 nm),[22] and hydrogen (486.46 nm)[23] were analyzed as a function of air pressure in the reactor and supplied RF power (Fig. 2).

The spectral line intensities of nitrogen and hydrogen increase linearly with increasing power. The spectral intensities of ionized forms of oxygen and argon increase particularly rapidly within the RF power range from 25 to 100 W. It seems that the increase in the RF field energy intensifies the ionization processes of oxygen molecules and after exceeding 100 W the state of equilibrium is reached. The content of various oxygen forms in the air plasma is considerable as indicated by numerous spectral lines with high intensities: 313.45, 375.36, and 380.27 nm.[25] As the pressure of air in the reactor rises from 0.07 to 0.2 Tr, the air plasma becomes more and more dense and unstable, especially at low induction powers, while the spectral intensity emitted by oxygen species is rapidly decreasing.

Water vapor plasma

The emission spectrograms of water vapor plasma (Fig. 1) indicate the presence of: OH radical (309.37
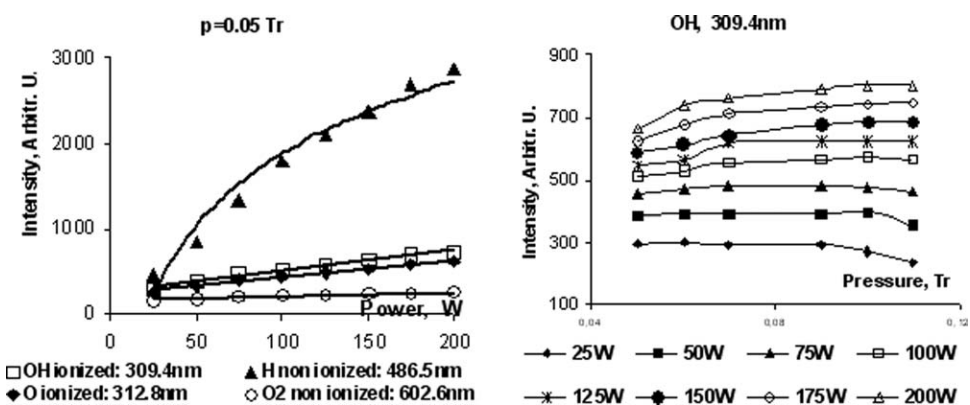

Figure 3 Changes in the optical emission intensity of water vapor plasma species as a function of power and pressure.
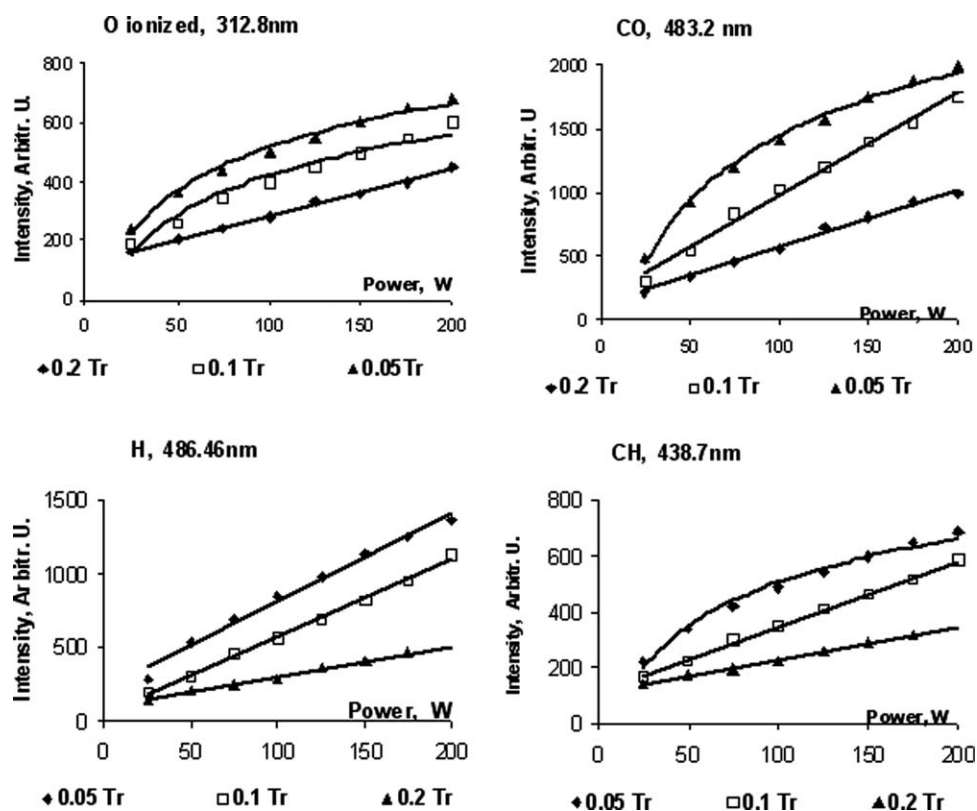
Figure 4 Optical emission spectrum of acetic acid plasma species as a function of power and pressure.

nm; 314.8 nm),[24,25] O_2^+ ions (312.8 nm).[22] The strong band at 486.46 nm identifies hydrogen in a nonionized state.[36] The spectrum of emission band shows no H_2O (616.5 nm),[22] which indicates the dissociated state of water vapor in plasma. Peyrous et al.[26] have modeled the elementary processes in the plasma of water vapor resulting in the formation of OH radicals and hydrogen atoms in the collision of water molecules with electrons as well as by means of atomic oxygen: $e^* + H_2O \rightarrow OH + H + e$; $O(^1D) + H_2O \rightarrow OH + OH$. The formation of OH radicals in plasma has been considered in several articles.[27–30]

Chemical species of plasma appear mainly in excited states and are transformed to the ground state by collision or radiation quantum emission (short lifetime of radicals).[26]

In the case of the highest intensity: 309.37 nm (OH) and 486.46 nm (H), the effect of process parameters on the spectral intensity was analyzed (Fig. 3).

Within the power range from 25 to 200 W and under pressure from 0.05 to 0.12 Tr, the same type of emission lines was observed; only the radiation intensity was changed. An increase in the power supplied to the reactor is accompanied by an increase in the intensity of emitted radiation being characteristic of the transformation of chemical species plasma. As the power is increased, hydrogen

atoms are rapidly generated (a rapid increase in the intensity of 486.5 nm band), which may be due to further decomposition of OH molecules into oxygen and hydrogen. Changes in the pressure level within the range from 0.05 to 0.12 Tr do not exert any significant influence on the spectral intensity of OH molecules.

Acetic acid vapor plasma

The emission spectrograms of acetic acid vapor plasma (Fig. 1) indicate the presence of the following radicals and ions: O_2^+ (282.4 nm), CO (297.7 nm), CHO (311.5 nm), O ionized (312.8 nm), CH (438.5 nm), CO (451.0 nm), CO (483.5 nm), CO (519.8 nm), CO (561.0 nm),[22] H nonionized (486.46 nm).[23] The chemical species of acetic acid vapor plasma appear mainly in excited states. Figure 4 shows the spectral intensities of CO (483.21 nm), O ionized (312.77 nm), CH (438.5 nm), and H nonionized (486.46 nm) as functions of power and pressure in the reactor. The increase in power intensifies the elementary processes in plasma (increase in the spectral intensity of chemical species). As the pressure of acetic acid vapor is increased, plasma becomes denser, and the spectral intensity of CO and O ionized, CH and H nonionized becomes lower.
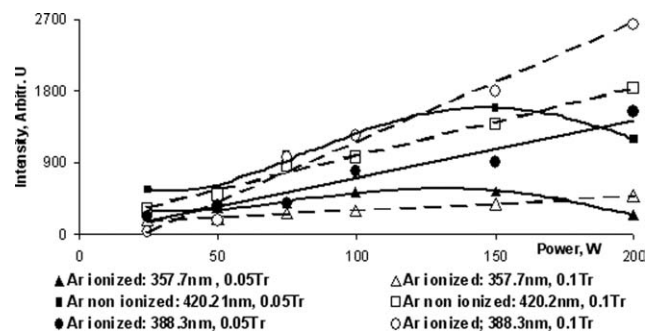
Figure 5 Optical emission spectrum of Argon plasma species as a function of power and pressure.

Argon plasma

The emission spectrogram of Ar plasma (Fig. 1) contains a large number of characteristic lines, which indicates a great susceptibility of argon to excitation. Ar ionized species are found within the short-wave range (330.4, 357.6, 371.3, 380.3, 388.29, 394.9, and 400.1 nm), while over 400 nm, the Ar species are nonionized (420.2, 433.65, 451.4, 522.6, 542.5, 565.6, and 591.7 nm). There are also present OH radicals (309.37 and 314.8 nm),[24,25] which indicate the presence of water molecules in the medium (in process gas or on the reactor walls).

Figure 5 shows the measurement results of the intensities of three characteristic Ar plasma lines as a function of discharge power and pressure. The increasing spectral intensity of the emission lines with increasing power indicates the intensification of elementary processes in this plasma (interactions between atoms and ions, interactions of excited particles, interactions between quanta and molecules as well as between neutral and excited atoms). The effect of plasma gas pressure is complex and diversified for the Ar species under consideration.

Surface chemistry

The chemical effects of plasma on the surface layer of PP film were assessed based on selective absorption of IR radiation. Examples of the absorption spectra of plasma-treated PP film (different treatment duration and power, pressure 0.05 Tr) are shown in Figure 6. The comparative analysis of the absorption properties of plasma-treated PP film surface indicates a new type of absorption within the wavelength range from 1640 to 1660 cm^{-1}. The maximum of absorption within this range is slightly shifted depending on the type of process gas. The maximum absorption of air plasma-treated PP is observed at a wave number of 1660 cm^{-1} and those of PP treated with acetic acid vapor plasma and water vapor plasma and Ar plasma–at 1645 cm^{-1} and 1640 cm^{-1} ($\lambda = 5.87$ μm), respectively. The

absorption of IR radiation within the range (1640–1660) cm^{-1} indicates carbonyl group ($>C=O$).[39] This new active center may be a result of the PP surface oxidation by the chemical species of plasma. The PP surface treated with Ar plasma shows also the presence of carboxyl groups. According to the opinion of the authors,[40,41] during the interaction between an inert gas and a polymer surface the main process consists in surface etching, while the effects of surface functionalization result from moisture absorption from surroundings when samples are removed from the reactor (post-treatment).[42]

In this study, the SEM images of PP film did not show changes in the topography of PP surface, thus the etching processes with Ar plasma in this case were limited. Consequently, the carboxyl groups on the surface of PP film seem to be generated during
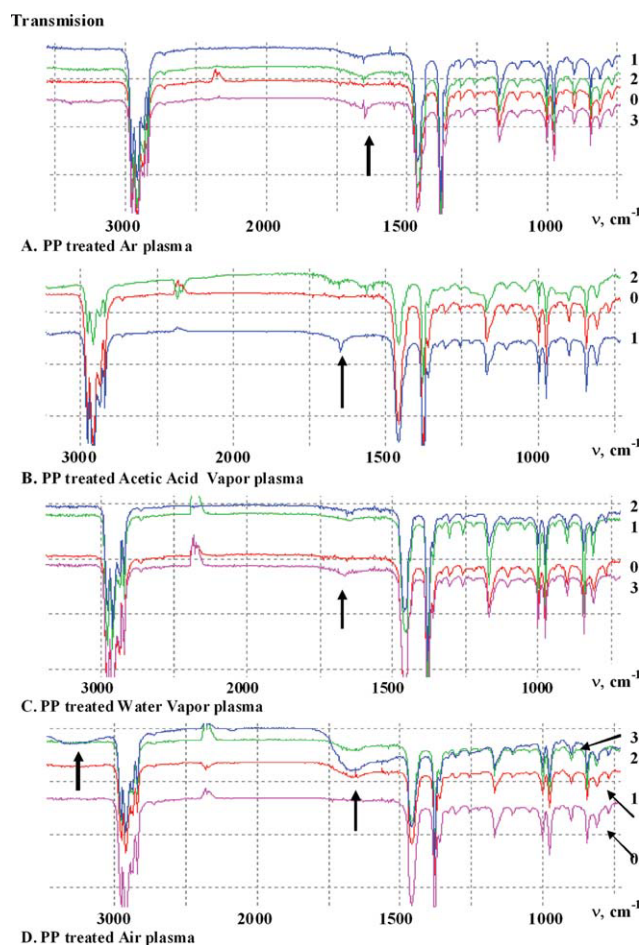

Figure 6 (A–D) ATR IR Absorption band of PP Cast films before and after oxidation, 0–PP untreated; A: PP treated Ar plasma $t = 10$ min, $p = 0.05$ Tr, 0.7 sccm, 1–100 W, 2–200 W, 3–300 W; B: PP treated Acetic Acid Vapor plasma: $t = 5$ min, $p = 0.05$ Tr, 0.7 sccm, 1–100 W, 2–300 W; C: PP treated Water Vapor plasma: $p = 0.05$ Tr, 0.7 sccm, $P = 300$ W. 1–3 min, 2–5 min, 3–15 min; D: PP treated Air plasma: $p = 0.05$ Tr, 0.7 sccm, $P = 50$ W. 1–1, 2–5, 10 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
% Atomic Concentration of Surface Composition of Plasma Treated PP Cast Films Obtained by XPS Measurements

Sample	O 1s	C 1s	N 1s	Si 2p
Untreated	1.5	98.4	–	0.1
Ar	7.0	91.3	0.8	0.9
Acetic Acid Vapor	14.8	82.7	1.0	1.5
Water Vapor	17.0	79.1	1.5	2.4
Air	8.6	81.9	8.7	0.8

the action of plasma OH radicals found in the optical emission spectrum (Fig. 1).

The level of absorption in the newly formed band depends on the plasma treatment conditions (process duration and power), process gas type and the physical micro-structure of PP film. The extension of treatment duration [Figs. 6(A–D): argon, air, water vapor] brings about an increase in absorption, so the number of functional groups formed on the surface is increased. An increased power brings about an increase in absorption. A further result of the plasma treatment is the disappearance of absorption band at 765 cm^{-1}. This band identifies the deformation vibration of methylene groups ($-CH_2-$).[39] The lack of this band would indicate etching processes and the elimination of polymethylene groups in the surface layer. This band disappears also by treating PP film with a saturated solution of chromic acid cleaning mixture.[4]

The PP surface treated with air plasma shows a new type of absorption with a maximum at 3300 cm^{-1}, especially after a prolonged treatment. The absorption within this range indicates the presence of hydroxyl and carboxyl groups.[28]

In the case of PP, AG being in the state of order and crystallinity, the use of ATR-IR method failed to find the absorption band of carbonyl group. It seems that the sensitivity of ATR-IR method is too low to detect the active centers with low concentrations.

A considerably better detection of chemical structure is provided by the X-ray Photoelectron Spectroscopy (XPS) technique that analyses surface layers of a thickness up to 10 nm. The measurement results of the chemical composition of PP surface layer by XPS are listed in Table I and shown in Figures 7, 8. The results are presented in a comparative system–for PP Cast film that was modified with various types of plasma at a constant power (100 W) and exposure time (10 min).

The initial polymer surface layer contains a low quantity of oxygen atom (1.5%) that considerably increases after the plasma treatments in the following media: Ar, air, acetic acid vapor, and water vapor. The treatment in the media used results in the oxidation of PP surface layer to an extent being dependent on the type of gas. Moreover, XPS spectra

have shown the presence of residual quantity of silicon Si—O (103.58 eV) and nitrogen C—N—O (401.26 eV) atoms that being combined with oxygen can influence the position of O peaks 1 s and cause some small departures from literature data. It is interesting to observe the considerable nitrogen content on the PP surface treated with air plasma, which is not any surprise, as nitrogen constitutes 78% of air, while oxygen content is only 21%. Nitrogen atoms durably combined with the polymer surface layer constitute with oxygen atoms active polar centers.

In this study, the state of oxygen and carbon atoms was analyzed on the basis of spectrum distribution into components (example of O spectrum 1 s is shown in Fig. 7 and C spectrum 1 s in Fig. 8).

The results show that oxygen can be present in C=O (532.22 and 287.5 eV), C—OH (533.02 and
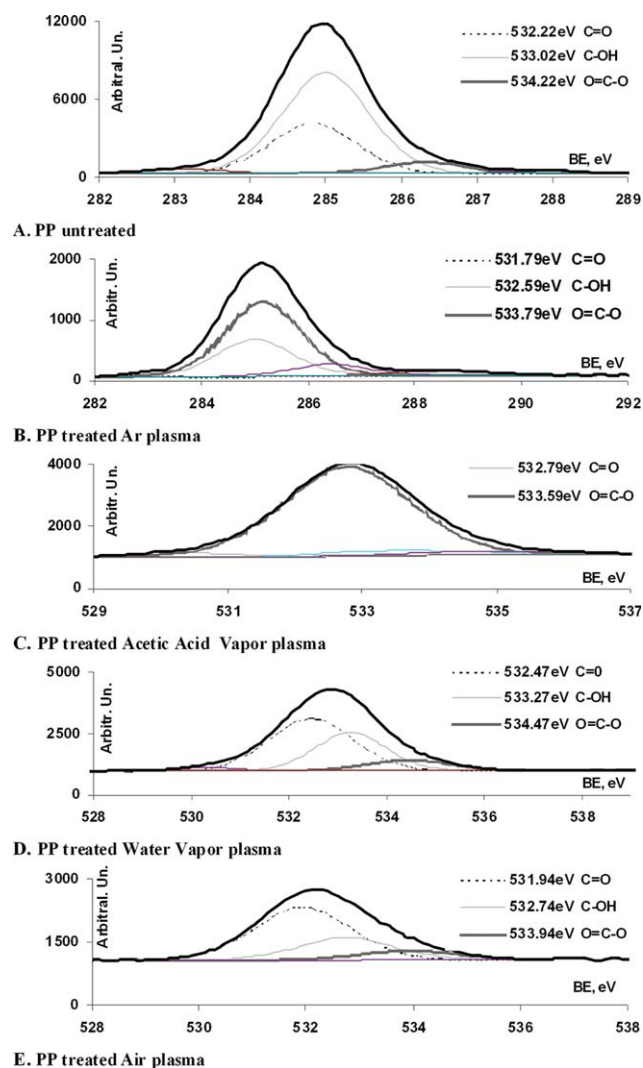

Figure 7 XPS O 1s spectra of plasma treated PP Cast (power 100 W and time 10 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
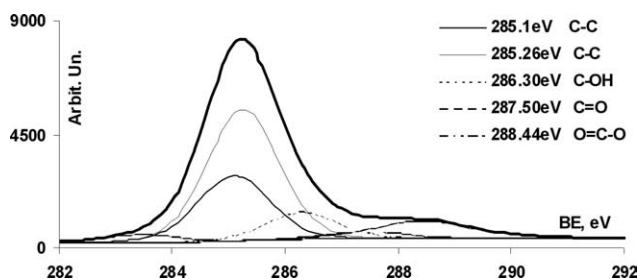
Figure 8 XPS C 1s spectra of Air plasma treated PP Cast (power 100 W and time 10 min).

286.3 eV), and O=C—O (534.22 and 288.44 eV) groups, which is consistent with the ATR-IR measurements. The identification of elementary peaks shows that in the PP surface layers treated with Ar plasma, dominating groups include O=C—O and C—OH, while in those treated with acetic acid vapor: O=C—O, in PP treated with water vapor: C=O and C—OH, and PP treated with air plasma: C=O groups.

Wettability

The wettability test of PP film surface indirectly indicates its susceptibility to molecular interactions with the liquid phase. Figure 9 shows a series of water drops deposited on the plasma-treated PP surfaces.

The shape of water drop meniscuses on the treated PP surfaces indicates an increase in the wettability of PP surface in each case of the process gas used. The quantitative evaluation of the PP surface susceptibility to wetting with liquids was made by means of the contact angle method, while the assessment of the interactions between molecules and the liquid phase was performed by means of surface energy components: polar and dispersive components. The test results are shown in Figures 10, 11 for PP films untreated and treated with plasma.

The treatment of PP film surface with plasma resulted in a decrease in the contact angles of PP with a liquid of an ionic character (water) as well as with a liquid of a dispersive character (methylene iodide). The quality of these changes depends on the type of process gas and on the treatment conditions (duration and discharge power). The improvement in the wettability of PP surface is obtained within a short time of the plasma-polymer interaction. The prolongation of the treatment over 1 min makes an insignificant progress in the further modification of physical and chemical properties of PP surface. The power of discharge influences very considerably the final effect of wettability–an increase in power results in decreased contact angles of PP surface in
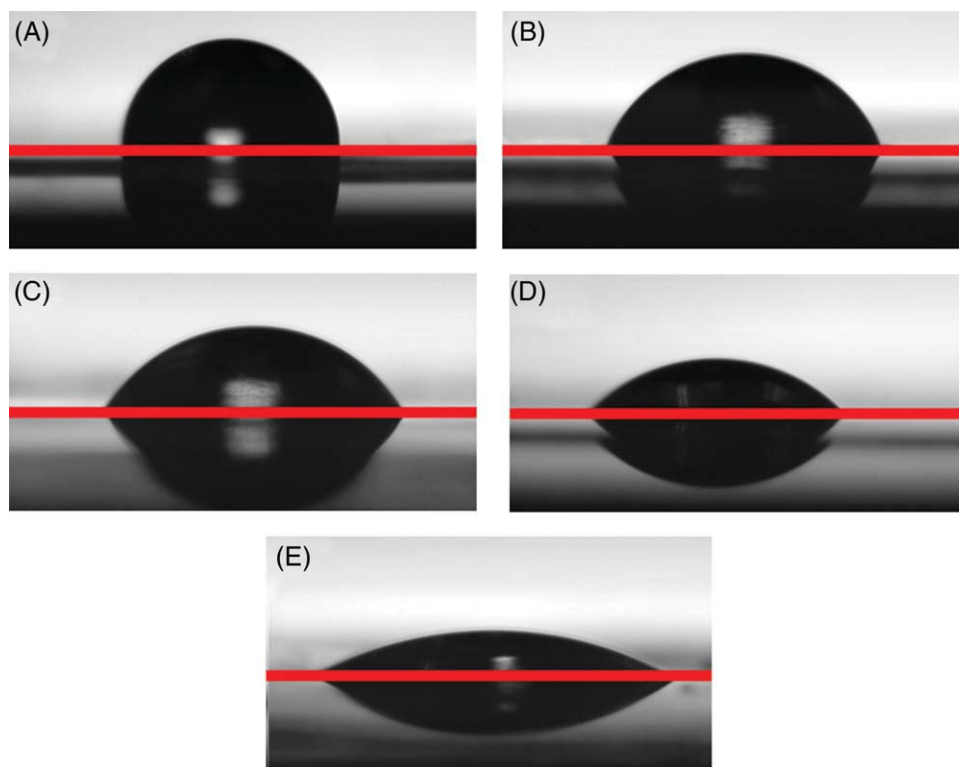

Figure 9 (AE) Images of water drops deposited on the untreated PP surface (A) and treated with Ar plasma (B), acetic acid vapor plasma (C), water vapor plasma (D), air plasma (E). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
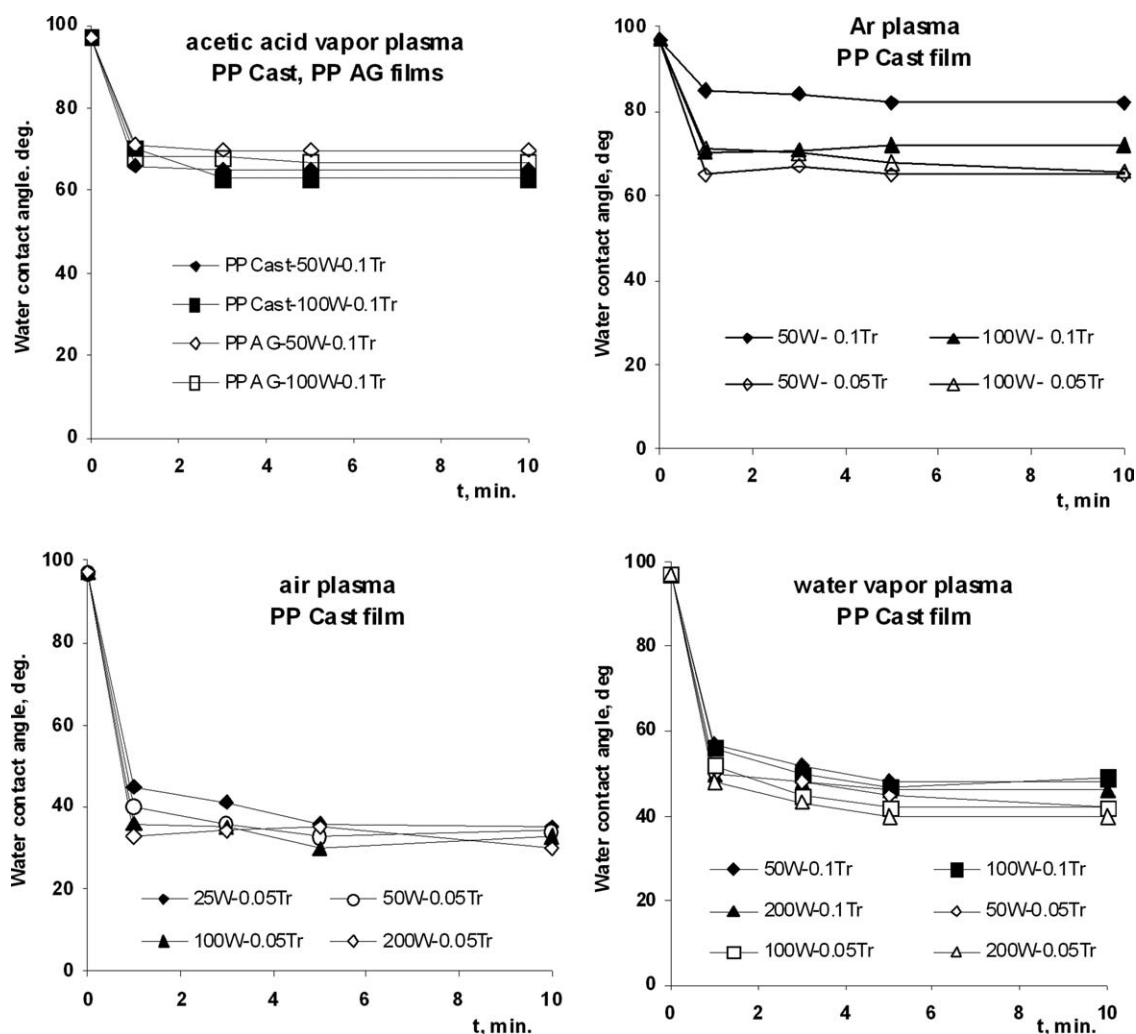
Figure 10 Changes in the water contact angle of PP surface modified with different plasma.

the case of both liquids. An improvement in surface wettability is also observed when the process gas pressure is reduced.

The power of discharge influences considerably the final effect of wettability–increasing the power from 25 to 300 W results in decreased contact angles of PP surface with either liquid.

The decrease in process gas pressure from 1 to 0.05 Tr leads to an improvement in surface wettability. The improvement in surface wettability depends to the largest extent on the type of process gas. The most significant decrease in contact angles was observed in the case of PP film surfaces treated with air plasma. For water, the contact angle is decreases to about 30° on the surface of PP treated with air plasma, to about 40° on surfaces treated with acetic acid or water vapor plasma and to about 70° on surfaces treated with Ar plasma. This kind of changes is in a direct relation with the state of chemical activity of the plasma-treated surface. The polar groups formed on PP surface by plasma treatment, confirmed by the FTIR-ATR examinations, intensify

the intermolecular interactions with the liquid phase, which is revealed by decreased contact angles or increased wettability.

The susceptibility of PP film surface to molecular interaction is characterized by the components of surface free energy (Fig. 11). Due to the lack of polar groups in PP, the polar component of surface energy of the untreated film is very low (~ 2 mJ/m^2). The dispersive interaction in a polymer mainly decides about surface energy; the dispersive component of surface energy is at a level of ~ 20 mJ/m^2. The dispersive interactions are considerably weaker and they are responsible for the low strength of adhesion of PP surface in two-phase systems.

The plasma treatment of PP surface brings about a slight increase in the dispersive component of surface energy. The plasma-treated PP can be lined up in order of increasing dispersive component: PP treated with Ar plasma < PP treated with acetic acid plasma < PP treated with water vapor plasma < PP treated with air plasma. The oxygen-containing groups created on the PP surface by plasma
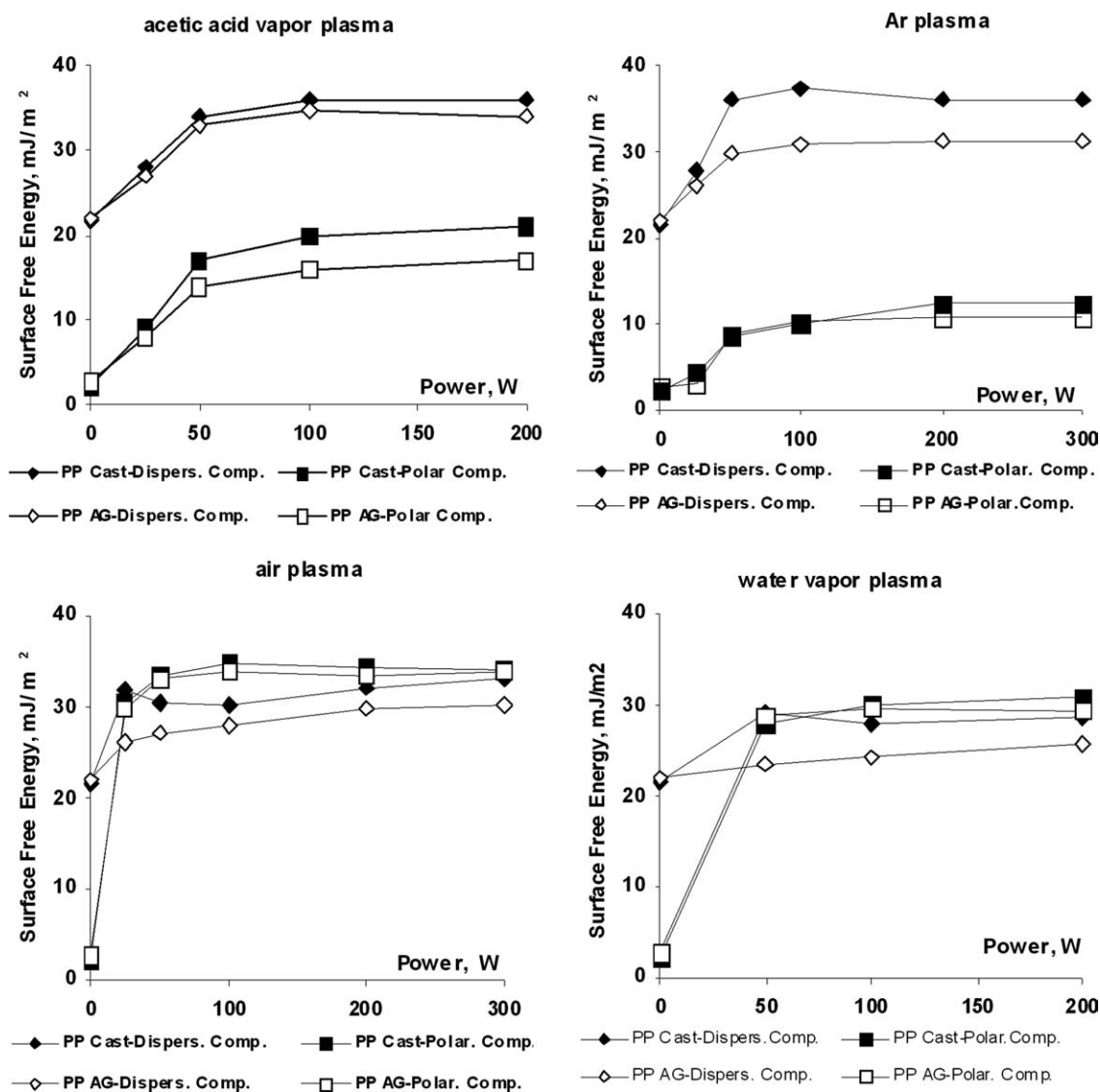
Figure 11 Changes in the surface energy of PP modified with different plasma, $p = 0.05$ Tr, $t = 10$ min.

treatment considerably increased the polar component of surface energy. Based on the results obtained, PP materials can be lined up in order of increasing polar component: PP treated with Ar plasma < PP treated with acetic acid plasma < PP treated with water vapor plasma < PP treated with air plasma. The results prove that the plasma treatment modifies the physical and chemical properties of PP surface to a larger extent than a chemical treatment.[4]

AFM analysis

XPS analysis suggested surface oxidation of plasma-treated PP films and the analysis of the surface morphology performed using SEM did not revealed any effects due to the plasma processing. So, AFM technique was used for the qualitative and quantitative comparison of the plasma-treated PP surfaces.

Figure 12 shows AFM topographic images for plasma treated Cast PP surfaces, after an exposure time (10 min) to the different plasmas at 100 W. All these images are 5000×5000 nm^2 with the corresponding z ranges given above the individual images.

PP surfaces treated with plasma are characterized by a high number of cavities in nano scale of different characters depending on the process gas used. The occurrence of different cavities indicates polymer surface etching. It is the surface treated with Ar plasma that is particularly strongly etched. This fact is consistent with papers by Kwon et al.[43] and Paynter[44] who indicate that Ar ions have a great activity in comparison to other process gases in interaction with a polymer surface. Paynter[44] has explained the particular coarseness of surfaces treated with plasma by the bombardment mechanism for PP surface.
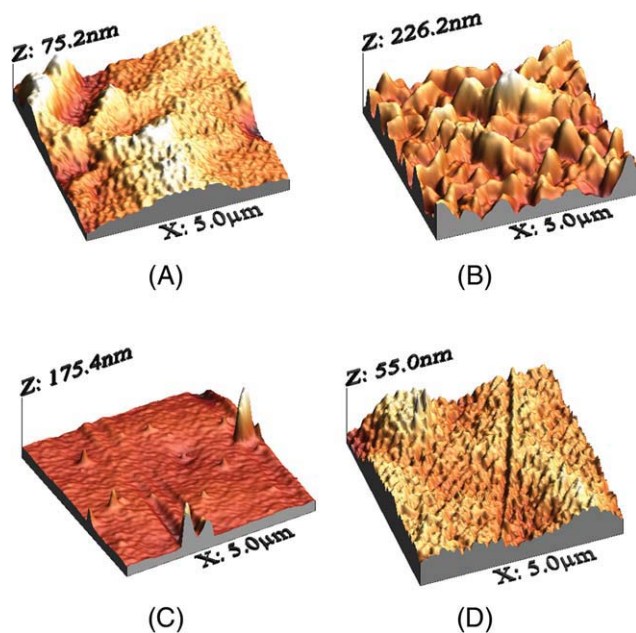
Figure 12 AFM images of PP Cast film. A: Air plasma treated at 100 W for 10 min. B: Ar plasma treated at 100 W for 10 min. C: Water vapor plasma treated at 100 W for 10 min. D: Acetic acid vapor plasma treated at 100 W for 10 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Changes in the morphology of the plasma treated polymer were quantified by root-mean-square (rms) surface roughness and surface area values. PP surfaces shown in Figure 12 are characterized by the following rms values: for acetic acid plasma-treated PP : 6 nm, for water vapor plasma-treated PP : 9 nm, for air plasma-treated PP : 13 nm, and for Ar plasma-treated PP : 33 nm.

The aging of plasma-treated PP films

The condition of surfaces of plasma-treated materials after removing them from the reactor to surroundings undergoes further transformations. The unneu-tralized chemical species (radicals, ions) in the surface layer of PP, in contact with gas and water vapor molecules contained in air, are neutralized for a long time after the termination of plasma treatment. This process, known as aging, can be controlled by assessing the physical and chemical properties of PP surface. The aging effect in this study was analyzed based on contact angle of water and methylene iodide deposited on PP surfaces treated with plasma and after a 6-month storage period.

Since the adhesive activity of a material surface depends mainly on the component polar free energy, Figure 13 shows now the changes in this component of PP film surface 6 months after the treatment. Both PP Cast and PP AG show the deterioration in polar properties of surface (decreased of the polar component of the surface energy). This ageing effect characterizes the surfaces treated with Ar, air, water vapor, and acetic acid vapor plasma. In each case, the polar properties of surface PP after aging are still better than that of untreated surface. One can assume that the new active centers created on the PP surface are stable.

Adhesive properties of PP films

The increase in the wettability of PP film surface obtained by plasma treatment directly points to an increased energy of its surface layer. In the new thermodynamic state, this surface is capable of stronger molecular interacting in contact with the other phase. These properties of surface interaction were assessed indirectly on the basis of adhesion forces by the T-Peel Test. Figure 14 shows the average values of adhesion forces measured in the standard adhesion tape-PP film system in comparison to those of untreated PP Cast and PP AG samples.

The plasma-treated PP film surfaces show stronger adhesive interactions in contact with the other phase. This effect occurs in PP films treated with all the types of process gas plasma. The adhesive
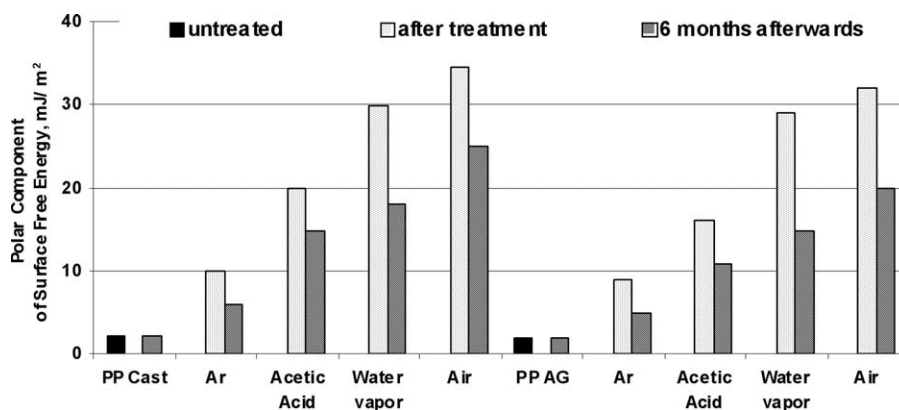

Figure 13 Aging of untreated and plasma-treated PP films: PP Cast and PP AG treated at Ar, Acetic acid vapor, water vapor, and air plasma environment ($p = 0.05$ Tr, 100 W, and 10 min).
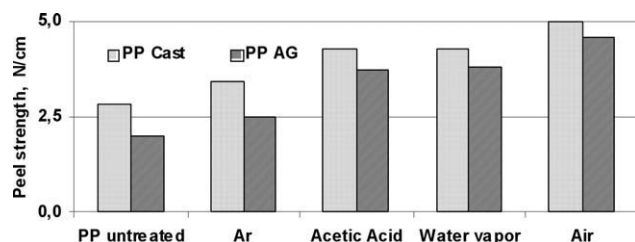
Figure 14 Peel strength of the PP film-tape system, PP film untreated and plasma-treated PP film (Ar, acetic acid vapor, water vapor, and air plasma: 0.05 Tr, 100 W, and 10 min).

properties of PP are most effectively modified by air plasma owing to the large number of active centers functional groups) created by this type of plasma on the PP film surface (FTIR-ATR results).

Effect of the fine structure of PP film

Under the conditions of PP film treatment with plasma, the surface etching processes were kept to a minimum and the dominating modification consisted in functionalizing the PP film surface. The effects of fine etching the PP surface in nano scale were observed in AFM images of different characters depending on the process gas used, particularly strongly etched is the surface treated with Ar plasma.

The tests performed showed a significant effect of plasma treatment on the physicochemical properties of both type of PP films (improvement in wettability, increase in the free energy of surface, increase in adhesion forces in contact with the liquid and solid phase). The results obtained indicate that the nonoriented and noncrystalline PP Cast film is more susceptible to plasma modification. The PP Cast polymer is characterized by a lower density and a lower energy of molecular cohesion and therefore, it is less resistance to the action of energetic species in the plasma medium in comparison to the semicrystalline polymer such as PP AG. The higher mobility of PP Cast particles in the surface layer conditioned by the fine structure better facilitates physical and chemical interaction with the particles of the second phase in contact.

CONCLUSIONS

- The surface of PP film was activated to prepare it for the deposition of thin organic layers. To provide a high adhesion of these layers to the PP substrate, new active centers were formed in the PP surface layer using various plasma types such as air, water vapor, acetic acid vapor, and Ar plasma.
- The chemical species of plasma were identified by the OES method. Based on the band inten-

sities of dominating species, one can assume that the intensity of elementary processes in plasma increases in the discharge of higher power and under a pressure below 0.1 Tr.
- The surface analysis results obtained by means of XPS show the presence of oxygen atoms of C=O, C—OH, and O=C—O groups in the plasma-treated PP surfaces. This state of surface oxidation results in the increase in the surface energy of the plasma-treated films, especially the polar component of this energy. The practical effect of the plasma modification of PP film is its increased wettability and stronger adhesive interactions in contact with a liquid and solid phase. Despite some ageing effect, the plasma-treated PP surface still shows an oxidized character, confirming the stability of the new active centers created on the polymer surface.
- The plasma media used can be ordered in a series of growing modification effectiveness: Ar plasma < acetic acid vapor plasma < water vapor plasma < air plasma.

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