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ARTICLE TYPE

Effect of cold plasma treatment on surface properties and gas permeability of polyimide films

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The surface functionalization of polyimide (Matrimid® 5218) films was carried out by cold plasma treatment with CF_4, N_2 and O_2 gases using a radio frequency discharge and the optimum plasma conditions were evaluated by water contact angle measurements. The surface hydrophobicity of polyimide films was obtained after CF_4 plasma treatment, while O_2 and N_2 plasma treatments contributed to the hydrophilic surface functionalization. X-ray photoelectron spectroscopy results revealed the presence of CF_x, amino or oxygen-containing groups attached to the polyimide film surface depending on the treatment gas. A strong influence of the used plasma gas on the film roughness was determined by atomic force microscopy measurements. The influence of the surface modification on CO_2, N_2 and O_2 gas permeation through the plasma treated films was evaluated. The permeation behaviour was characterized in terms of transport parameters, namely, coefficients of permeability, diffusion and solubility. The permeability coefficient of all plasma treated polyimide films for the studied gases (CO_2, N_2 and O_2) was found to decrease following the order of increasing the kinetic molecular diameter of the penetrant gas. Besides, the selectivity coefficient was found to be significantly increased after the plasma treatments – $\alpha_{CO2/N2}$ was increased up to 36 % and 98 % for O_2 and N_2 plasma treated Matrimid® 5218 films, respectively. The relationship between the gas permeation behaviour and the surface modification of polymer film by cold plasma was discussed.

Introduction

Thanks to a number of significant properties such as excellent thermal and thermo-oxidative stability, solvent resistance, as well as fire retardant, mechanical and electrical properties, the aromatic polyimides have extensive applications in various fields ranging from aerospace to microelectronics, composites and fiber optics.[1-5] Polyimides are also an important class of polymers for gas separation membrane.[6-9] However, applications of polyimides are limited by their hydrophobic surfaces, which results in poor wettability and poor adhesion.[1,10] The commercially produced 3,3'-4,4'-benzophenone tetracarboxylic-dianhydride diaminophenylindane (BTDA-DAPI), commonly known as Matrimid® 5218 (Fig. 1), is a thermoplastic polyimide widely used due to its high glass transition temperature (T_g = 323 °C) and good processability.[5,6] Matrimid® 5218 is also interesting as a polymer for gas separation membranes because it is readily soluble and exhibits an excellent combination of selectivity and permeability for many significant gas pairs.[5,6,9] The selectivity and permeability of Matrimid® 5218 are superior to those of most other commercial polymers.[11]

The methods most widely used to modify the surface of polymers are chemical treatment, electrochemical treatment, photo-irradiation and plasma treatment.[10,12-17] For example, poly(ethylene)oxide was introduced in Matrimid® 5218 by the cross-linking method.[11] It was found that such cross-linked polyimide membranes displayed excellent CO_2 permeability and CO_2/N_2 selectivity.[11] The electrophilic bromination on the aromatic ring of Matrimid® 5218 was reported by Guiver et al.[17] The 1.6-fold increase in gas permeabilities for O_2 and CO_2 with some concurrent decrease in permselectivity of 7-8 % for O_2/N_2 and CO_2/CH_4 gas pairs was established owing to the decreased chain mobility in the presence of bulky bromine atoms. The presence of the bulky trifluoromethyl group in both amine and anhydride moieties of poly(ether imide) membranes leads to the decrease of the local segmental mobility and to the increase of the free fractional volume and helps to achieve excellent permeability as well as reasonably good selectivity.[3] The other approach to improve the gas permeability of polyimide is to combine it with the conducting polymer (polyaniline), i.e. to synthesize the so-called dopable polyimide.[18] In this case 2.4-fold increase in O_2/N_2

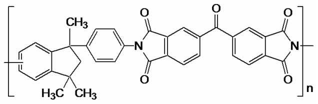

Fig. 1. Chemical structure of Matrimid® 5218.

permselectivity compared with a conventional nondopable polyimide was revealed due to the polymer free volume reducing by the dopant molecules.

It is known that the surface of polymers can be modified by plasma composed of various reactive species, including free radicals and ions. There are two principal advantages in using plasma treatment for polymers. One advantage is that the reaction takes place only on the surface of the polymer without significantly changing its bulk properties. The other one is that it is possible to change (increase or decrease) surface energy, to produce specific functional groups on the surface, to modify surface morphology, i.e. surface crystallinity and roughness. Plasma treatments of polymers have come to be extensively used because of their very high efficiency and operational simplicity.[10,13,14] For example, it has been shown that the low pressure plasma treatment with a gas mixture of 70 % Ar and 30 % O_2 significantly improves the adhesion of copper layer on polyimide surface.[13] Yang et al. have also shown that the copper film growth increases after nitrogen and oxygen plasma pre-treatment of polyimide films because of the surface energy reducing.[19] The effect of tetrafluoromethane (CF_4) plasma treatment on the interfacial energy of Ag/polyimide system was investigated by Park et al.[20] It was found that because of the mechanical interlocking effect that increased the surface roughness through the incorporation of hydrophobic fluorine-based functionalities, the adhesion of the metal/polymer system was enhanced.[20]

Therefore, one can suppose that the surface modification by plasma treatment provides a promising approach for controlling the transport properties of gases through polyimide films due to the changes in the surface polarity (hydrophobic/hydrophilic balance), the grafting of interactive chemical groups (for example, CO_2 affinity) or modifications of the surface roughness.[13,15,19-24] However, this approach is not studied sufficiently and the better understanding of the relationship between surface and transport properties of plasma treated membranes is needed.

Taking into account the fact that polyimide is very promising material for gas separation due to its selectivity and high thermal and mechanical stability, in the present work the surface of Matrimid® 5218 film was treated by using CF_4, N_2 and O_2 plasmas in order to change polyimide selectivity. The objective of this work was to find relationship between the surface modification of Matrimid® 5218 film and its gas permeation properties. Initially, the plasma parameters (radio frequency (RF) power, gas flow and treatment time) for each gas used were optimised on the basis of water contact angle measurements. Then, the changes in the surface properties of the plasma treated polyimide membranes were characterized by AFM and XPS measurements. Finally, the modification of the values of gas permeability towards N_2, O_2 and CO_2 resulting from different plasma treatments was analysed.

Experimental

Materials

The Matrimid® 5218 powder was kindly donated by Huntsman (Switzerland) and stored in a dry place. The organic solvent, N-methyl-2-pyrrolidone (NMP) (99% purity), was purchased from Acros Organics. The gases used for plasma treatment (CF_4, O_2 and N_2) and for gas permeation experiments (CO_2, O_2 and N_2) with a purity of 99.99 % were purchased from Air Liquid and Messer (CF_4 gas) and used as received.

Matrimid® 5218 film preparation

Dense polyimide films were prepared via a solution-casting technique. Initially, the polymer powder was being dissolved in NMP solution (150 g/L) under stirring at 70 °C during 7h. Then, the obtained viscous solution was cast on a glass plate using a Doctor Blade in order to ensure a final film thickness of 80-100 µm. The cast membranes were placed in a temperature-controlled vacuum oven for the thermal treatment.[7] To remove the residue solvent, the membranes were vacuum dried at 65 °C for 3h, then at 95 °C for 15h and then at 170 °C for 48h. Finally, the membranes were dried in oven at 200 °C for 48h. After the thermal treatment the membranes were removed from the oven and stored in a desiccator over P_2O_5 at room temperature (23 ± 2 °C).

Plasma treatment of Matrimid® 5218 films

The plasma modification was carried out in RF plasma reactor, which was driven by a 13.6 MHz generator (Sairem 0-600 W), with a matching box adjusting the generator impedance to limit the reflected power. The reactor was a 310 mm × 255 mm rectangular aluminium chamber with the rectangular cathode (100 mm × 210 mm) linked to the generator and the grounded anode. A primary pump (CIT-ALCATEL Pascal N 2010 SD) and a turbomolecular pump (ALCATEL ATP 80/100) allowed obtaining a base pressure in the reactor of 10^{-7} mbar. Mass flowmeters (Aera FC 7700 CDC) controlled the amount of injected gas. In this type of reactor the pressure depends on the gas flow. When the chamber pressure was stabilized, RF power was applied to create plasma. After the plasma modification, RF power was turned off. Vacuum was broken by opening a valve to admit air into the chamber. Once the chamber pressure reached atmospheric pressure (typically within 5 min), the plasma modified Matrimid® 5218 film was taken out for further characterization. In order to define optimum plasma conditions three different plasma parameters were tested: gas flow (from 5 to 40 standard cm^3/min (sccm)), RF power (from 10 to 100 W) and the treatment time (10 – 600 s). Both sides of the membrane were treated one by one and each film side was analyzed. The reproducibility of films was tested by replicating the plasma treatments.

Surface characterization methods

Water contact angle measurements. The contact angle of water droplets was measured using a goniometer Rame-Hart N 100-00 (visual reading) at room temperature (23 ± 2 °C). For each measurement a 5 µL drop of water (milli-Q Water System, resistivity 18 MΩ/cm) was formed at the tip of the syringe. After the water dripped onto the surface of the plasma treated polyimide film, the contact angle was measured within 5 s by a sessile drop method. For each sample five water drops were placed at different locations distributed uniformly on the film surface and the average value of measurements was calculated.

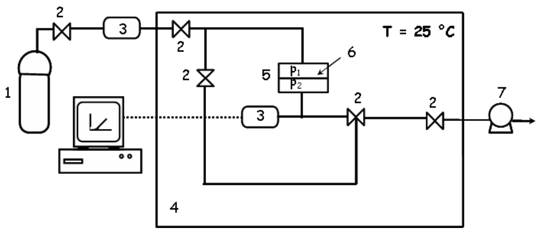

Fig. 2. Schematic diagram of the gas permeation experimental setup: *1* – gas cylinder; *2* – stop valve; *3* – pressure controller; *4* – oven; *5* – permeation cell; *6* – polymer film; *7* – vacuum pump.

Atomic force microscopy (AFM). The surface morphology of the plasma treated membranes was observed by atomic force microscopy using a Nanoscope IIIA (Veeco – Digital instruments, California, USA). The imaging process was performed in tapping (intermittent contact) mode in air at room temperature (23 ± 2 °C). The piezo-scanner used was a J-type (100 µm scan range). The microcantilever used had a resonance frequency of about 300 kHz. The tip was a standard tip made of silicon.

X-ray photoelectron spectroscopy (XPS). The chemical nature of the treated membranes was measured by XPS analysis using a 250 Xi Escalab photoelectron spectrometer (Thermo VG, United Kingdom). The spectrometer was equipped with a monochromatic Al Kα X-ray source generating photons with the energy of 1486.6 eV. Survey and high-resolution spectra were collected with pass energy of 50 eV and 20 eV, respectively. Analysis of XPS spectra was performed by peak fitting using the data processing tool of Avantage system. The C_{1s} peak at 285.0 eV was used as an internal reference to other peaks. XPS spectra were fitted by using Gaussian-Lorentzian function. A linear background was subtracted before peak fitting. Atomic composition was calculated using peak area.

Gas permeation measurements. The pure gas permeation properties were evaluated by a variable-pressure constant-volume method, i.e. the "integral permeation" method, using home-made apparatus (Fig. 2). This method is based on continuous monitoring of the amount of penetrant diffusing through a membrane into a closed vessel, where p_1 and p_2 (Fig. 2) are the pressure in supply volume (upstream side) and receiving volume (downstream side), respectively.[25] The permeation process can be divided into the transient and steady state stages. The transient or dynamic stage can be represented by the so-called time lag parameter (t_L). The value of this parameter can be obtained from the extrapolation of the steady-state line on the time axis.

The plasma treated polyimide film (25 × 52 mm^2) was mounted in the stainless permeation cell (effective area of the film: 4.94 cm^2), which was then completely evacuated by applying a vacuum (10^{-3} mbar) on both sides of the film during the period of time at least twice the duration of measurement. Then, the upstream side was supplied with the tested gas at pressure p_1 = 4 bar (absolute pressure). The increase of pressure in the calibrated downstream part (p_2) (Fig. 2) was measured by a sensitive pressure gauge (0 – 10 mbar, Druck AW 10 T4) linked to a data acquisition system. The gas permeation measurements were performed at 25 °C in a thermoregulated chamber.

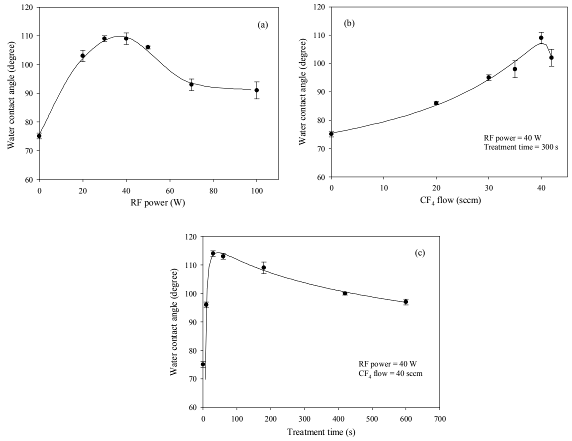

Fig. 3. Water contact angle of Matrimid® 5218 surface treated by CF_4 plasma as a function of (a) RF power, (b) CF_4 flow and (c) treatment time.

The gas permeability coefficient (P) was calculated using the variable pressure method,[7] assuming $p_1 >> p_2$:

$$P = \frac{J_{st} d}{p_1}, \qquad (1)$$

where d is the film thickness and J_{st} is the steady-state gas flow obtained from the slope of the steady-state part of the curve of pressure p_2 versus time.The time lag diffusion coefficient (D) was calculated from the time lag value t_L given by the extrapolation of the linear steady-state portion to the time axis:

$$D = \frac{d^2}{6t_L}. \qquad (2)$$

The solubility coefficient (S) was determined as a ratio of the permeability to diffusion coefficient:

$$S = \frac{P}{D}. \qquad (3)$$

The selectivity coefficient ($\alpha_{A/B}$) was defined as the ratio of the permeability coefficients determined for gases A and B:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A S_A}{D_B S_B}. \qquad (4)$$

Each pure gas (N_2, O_2 and CO_2) was tested. The permeation measurements were performed four times for the same sample for each gas and for two other samples to ensure reproducibility of results. The permeation parameters (P, D and S) were obtained with the precision from 2 % to 10 %. The upstream pressure (p_1 = 4 bar) applied to the samples and the order of gases' passage (N_2, O_2 and CO_2) were chosen so that no irreversible plasticization modification of the polymer occurs, in particular by CO_2.[7,8]

Results and discussion

Optimisation of plasma parameters

The aim of the plasma treatment was to obtain the film surface with either hydrophobic (by CF_4 plasma treatment) or hydrophilic (by N_2 or O_2 plasma treatments) character. For this purpose the non-thermal, so-called cold plasma, was used and three different plasma parameters for each gas were tested: gas flow (D_f), RF power (P_w) and the treatment time (t). In general, cold plasma is any plasma which is not in thermodynamic equilibrium because either the ion temperature is different from

Table 1. Optimized plasma conditions for Matrimid® 5218 film.

	Untreated film	CF_4 plasma treated film	N_2 plasma treated film	O_2 plasma treated film
Optimum plasma parameters		P_w = 40 W D_f = 40 sccm t = 30 s pressure = $1.2 \cdot 10^{-2}$ mbar	P_w = 80 W D_f = 10 sccm t = 120 s pressure = $1.4 \cdot 10^{-4}$ mbar	P_w = 70 W D_f = 15 sccm t = 180 s pressure = $0.8 \cdot 10^{-4}$ mbar
Water contact angle value θ_w (degree)	75 ± 1	114 ± 1	≤ 10	≤ 10

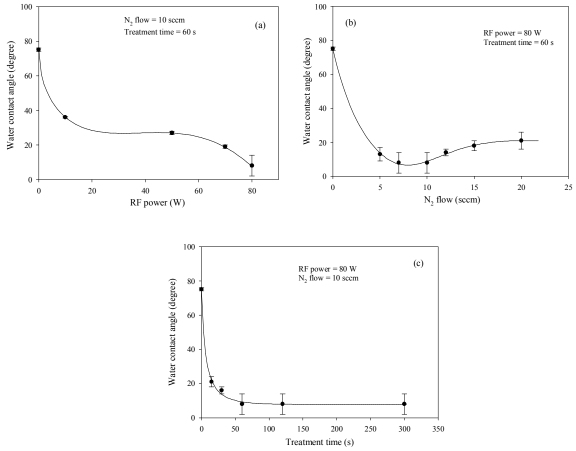

Fig. 4. Water contact angle of Matrimid® 5218 surface treated by N_2 plasma as a function of (a) RF power, (b) N_2 flow and (c) treatment time.

the electron temperature or the velocity distribution of one of the species does not follow a Maxwell-Boltzmann distribution.[13] One of the simplest methods for determining the changes in hydrophobicity that take place in the outermost layer of film after a modification process is the contact angle measurement. So, the optimisation process of plasma parameters was performed on the basis of water contact angle measurements.

In the case of CF_4 plasma modification the optimization process is in defining for each parameter (gas flow, RF power and the treatment time) the value corresponding to the highest hydrophobicity, i.e. the highest water contact angle value. To optimize each of these parameters, only one varied while the others were kept constant. Initially, the plasma process was carried out at a fixed flow rate of 40 sccm and a treatment time of 5 min; RF plasma power was varied from 20 W to 100 W (Fig. 3a). The obtained results indicate that Matrimid® 5218 surface became more hydrophobic and that the sharp increase of the water contact angle (from 75 ° on virgin membrane to 114 ° on plasma treated membrane) took place for RF power less than 40 W. Then, the water contact angle started to decrease with the increase of RF power up to 70 W and finally reached a steady value 95 ° at 100 W.

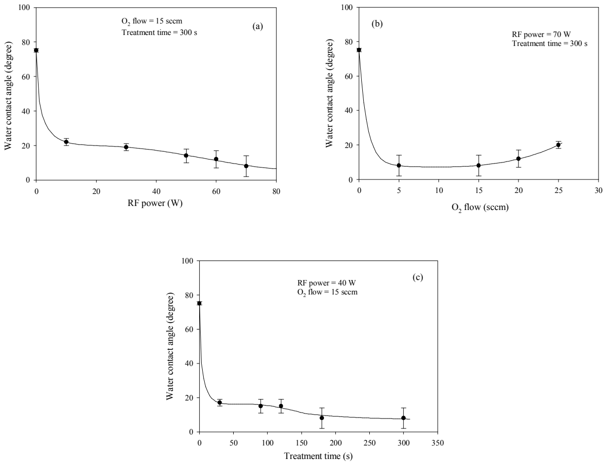

Fig. 5. The water contact angle of Matrimid® 5218 surface treated by O_2 plasma as a function of (a) RF power, (b) O_2 flow and (c) treatment time.

The water contact angle values of Matrimid® 5218 surface as functions of CF_4 gas flow and the treatment time are shown in Fig. 3b and 3c, respectively. One can see that in both cases the water contact angle values increased at the beginning with the increase of gas flow or plasma duration. However, the further increase of gas flow (more than 40 sccm) and the treatment time (longer than 30 s) provoked a decrease of water contact angle values (Fig. 3b and 3c). The optimum parameters for CF_4 plasma treatment are presented in Table 1. It should be noted that the plasma treatment during only 30 s is sufficient enough to obtain the polyimide membrane with remarkable hydrophobic character (Fig. 3c and Table 1).

It is known that the major reaction mechanism of CF_4 plasma treatment is a simultaneous degradation and fluorination process.[22,26] On the basis of the obtained results (Fig. 3), one can conclude that before reaching the optimum plasma parameters (Table 1) the fluorination is a dominating process, since the hydrophobic character of Matrimid® 5218 surface increases. This corresponds to the grafting of fluorinated species formed during plasma treatment to the polyimide surface. However, after the optimum values of CF_4 plasma modification are reached, the degradation process begins to dominate. The active sites generated on the polymer membrane surface after CF_4 plasma treatment may further react with oxygen and water in air to form oxygen-containing groups after the plasma modification is stopped.[22] Hence, the hydrophobic character of Matrimid® 5218 surface is lost and the decrease of water contact angle value is observed (Fig. 3).

N_2 and O_2 plasma treatment is known to improve the surface hydrophilicity.[19,23,24,27,28] Thus, the optimization process in this case consists in the determination of the value for each parameter (RF power, gas flow and the treatment time) that gives the lowest water contact angle value. Fig. 4 shows the water contact angle value of the N_2 plasma treated Matrimid® 5218 film as a function of plasma operational parameters (RF power, N_2 flow and the treatment time). The results exhibit that the hydrophilicity of membrane surface after exposure to the plasma increases greatly. In the case of O_2 plasma treatment (Fig. 5) the same picture is observed, i.e. a sharp decrease of the water contact angle values from 75 ° for virgin film surface up to ~ 10 ° (complete wetting condition) after plasma treatment. The decrease of the contact angle values could be caused by the presence of hydrophilic groups in the plasma treated layer. Furthermore, the amount of these groups depends on the plasma conditions. The optimum conditions for N_2 and O_2 plasma treatments are summarized in Table 1.

The decrease of the water contact angle value may be provoked by the following reason. N_2 plasma is less aggressive than oxidizing plasmas (for example, O_2 plasma). The main effect of N_2 plasma treatment is surface functionalization by the insertion of different polar groups. The different species presented in N_2 plasma (such as N_2^+, N_2^* (excited), N, N^+, electrons) have been found by means of optical emission spectroscopy.[29] These species can excite the polymer surface and break C-C (C-H) bonds (Fig. 1), i.e. create polymer excited sites. This is followed by the reaction with N_2^* in plasma or with oxygen in air since the vacuum levels do not guarantee total absence of oxygen impurities in the reactor chamber,[30] these being highly reactive. These consecutive reactions can make new functional groups such as amine, amide, ether, carboxyl and carbonate groups related to nitrogen and oxygen on surface. Therefore, as the number of N_2^* and N_2^+ excited states increases in plasma atmosphere with RF power and gas flow increasing (Fig. 4a and 4b), atomic fractions of oxygen and nitrogen incorporated in polyimide surface are expected to increase with corresponding water contact angle value decreasing. Also, one can observe that the longer the treatment time is, the lower the water contact angle value is (Fig. 4c).

On the other hand, O_2 plasma treatment generates reactive surface groups, such as ketone, ester and carboxylic acid functionalities, that can arise from bond scission and insertion processes.[31] Besides, it should be noted that O_2 plasma functionalization is accompanied by the etching process. Naddaf et al. have shown the influence of time of exposure to O_2 plasma on the weight of polyimide film.[32] It is found that the weight loss of polyimide film increases as the treatment time increases. This weight loss was attributed to the sputtering of the surface by the incident oxygen species, in particular, by atomic oxygen.[32] So, the slight increase of the water contact angle value with N_2 and O_2 flow increasing (Fig. 4b and 5b, respectively) may be explained by the chemical sputtering, in which highly reactive species of the plasma interact with near-surface polymer chains and break the weakly bonded elements into volatile chemical species, which, in its turn, can be deposited again on the film surface or pumped out. Also, starting with a certain value, the further increase of the gas flow does not increase the concentration of the reactive species since the electron density is kept constant as it is controlled by the power parameter. It means that even if the flow increase provokes the increase of the molecules' quantity in the plasma phase, the number of the electrons and, thus, the effectiveness of the plasma treatment generally decrease. Therefore, the surface chemistry is not enhanced and remains as observed at a lower flow. That's why a slight increase of the water contact angle is observed for the hydrophilic plasma treated polyimide films.

Therefore, contact angle variations observed for Matrimid® 5218 after CF_4, N_2 and O_2 plasma treatments may be explained by variations in the chemical composition and/or roughness of the surface. The chemical composition was studied by XPS, while roughness variations were observed by AFM measurements.

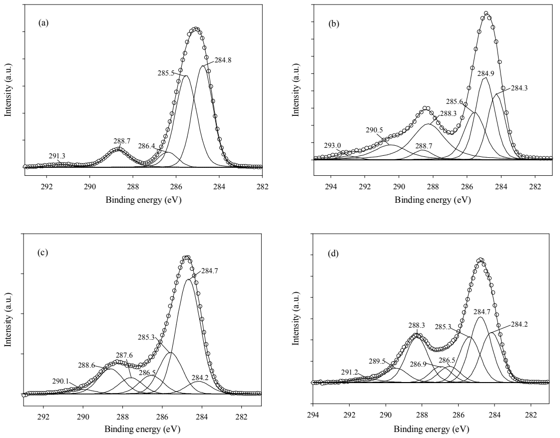

Fig. 6. High resolution C_{1s} XPS spectra of Matrimid® 5218 film: (a) untreated film, (b) CF_4 plasma treated film, (c) N_2 plasma treated film, (d) O_2 plasma treated film.

Surface characterization of Matrimid® 5218 films

Cold plasma treatment usually modifies extreme surface of polymer membranes, but in some cases it can slightly change the crystallinity of a polymer material by increasing temperature.[26] So, in order to examine the influence of the plasma treatment on Matrimid® 5218 film structure, ATR-FTIR, thermogravimetric (TGA) and DSC measurements were performed (not shown). It was found that the Matrimid® 5218 film is stable up to 450 °C and the glass transition temperature (T_g) is close to 322 ± 1 °C. However, the performed measurements didn't detect any change in obtained data after the plasma surface modification as the modified polymer depth (~ 10 nm) was less than the ATR-FTIR depth (1-2 μm). Besides, the thermal measurements had less sensitivity to the surface phenomenon because of the large amount of product used (~ 10 mg). Therefore, the changes induced by the plasma treatment were characterized by the surface analysis, i.e. XPS, AFM and water contact angle measurements.

XPS analysis. Information on how fluorine, nitrogen and oxygen are bound to the polymer surface can be obtained from the XPS spectra. Fig. 6 presents high resolution C_{1s} spectra of Matrimid® 5218 films after different plasma treatments. The C_{1s} spectrum for the untreated membrane is given for comparison (Fig. 6a). Table 2 presents the surface composition determined from XPS analysis.

The C_{1s} core-level spectrum of untreated Matrimid® 5218 film is fitted in five peaks (Fig. 6a), that can be attributed to five types of polyimide bonds: C-C bond (284.8 eV), C-H bond (285.5 eV), C-N bond (286.4 eV), carbonyl group (C=O) in imide rings (288.7 eV) and small π-π^* shake-up satellite peak at 291.3 eV evidencing of the aromatic ring in the polymer. These assignments are in excellent agreement with the previous results obtained for the pure polyimide films.[33-35]

The C_{1s} peak shows a change in the peak position and intensity after film exposure to plasma (Fig. 6 (b-d)). After CF_4 plasma treatment the significant amount of fluorine (20 at.%,

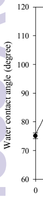

Table 2. Elemental composition (at. %) of Matrimid® 5218 surface as a function of the plasma treatment.

	Untreated film	CF_4 plasma treated film	N_2 plasma treated film	O_2 plasma treated film
C_{1s}	84	59	66	64
O_{1s}	12	18	24	30
N_{1s}	4	3	10	6
F_{1s}	-	20	-	-
O/C	0.14	0.30	0.36	0.47
N/C	0.05	0.05	0.15	0.09
F/C	-	0.34	-	-

Table 2) is found on the membrane surface. Besides, a dramatic change in C_{1s} core-level spectrum is observed (Fig. 6b), which can be attributed to the formation of fluorinated carbon functionalities:[21,22, 34, 36] CF_2-CH_2 bond at 285.6 eV, C-F bond at 288.3 eV, CF_2-CF_2 bond at 290.5 eV and CF_3-groups at 293.0 eV. It is known that the aromatic shape-up satellite signal (π-π* transition) presented in C_{1s} core-level spectrum is very sensitive to the chemical environment of the aromatic groups.[22,27] Therefore, the disappearance of this signal in the case of CF_4 plasma treated film (Fig. 6b) testifies that the aromatic groups are attacked by the plasma formed species.[22,37] Wheale et al. have shown that the fluorination across carbon-carbon double bonds (-CH=CH-) is strongly favoured from a thermodynamic perspective.[37] In this case atomic fluorine ($F^{\cdot}$) reacts with the carbon-carbon double bonds resulting in the substitution of hydrogen by fluorine and generating a reactive radical site (-$C^{\cdot}$H-CHF-). This radical can be also subsequently fluorinated by atomic fluorine to form (-CHF-CHF-). In its turn, the remaining hydrogen atoms may be fluorinated according to the same radical mechanism providing the formation of fluorinated carbon functionalities, such as CF_3, CF_2-CF_2, CF_2-CH_2. Besides, some decrease of the carbon content (59 at.% in comparison with 84 at.% for untreated film) was revealed (Table 2). Also, F/C ratio for CF_4 plasma treated polyimide was found to be equal to 0.34 (Table 2). The slight decrease of the nitrogen content (3 at.% compared to 4 at.% for untreated membrane) as well as the disappearance of the peak at 286.4 eV (C-N bond) (Fig. 6b) may be explained by the attack of CF_4 species at nitrogen-containing functionalities to form gaseous by-products containing C-N linkages.[15,37] It has been already shown that the imide ring in polyimide is easy to break during the plasma treatment.[15] The scission of the imide bonds leads to the formation of reactive radicals that are able to form fluorinated functionalities. Therefore, Matrimid® 5218 surface after the plasma fluorination seems to appear as a Teflon-like structure. The elemental composition of the membrane surface (Table 2) as well as the decomposition of C_{1s} spectrum (Fig. 6b) can be explained by the fact that active radicals lead to the formation of relatively strong carbon-fluorine bonds on Matrimid® 5218 film. The presence of these fluorinated groups provides a hydrophobic character of CF_4 plasma treated membrane (Fig. 3 and Table 1).

In the case of N_2 and O_2 plasma treatments it was supposed that the improved wettability (Fig. 4 and 5, Table 1) was reached

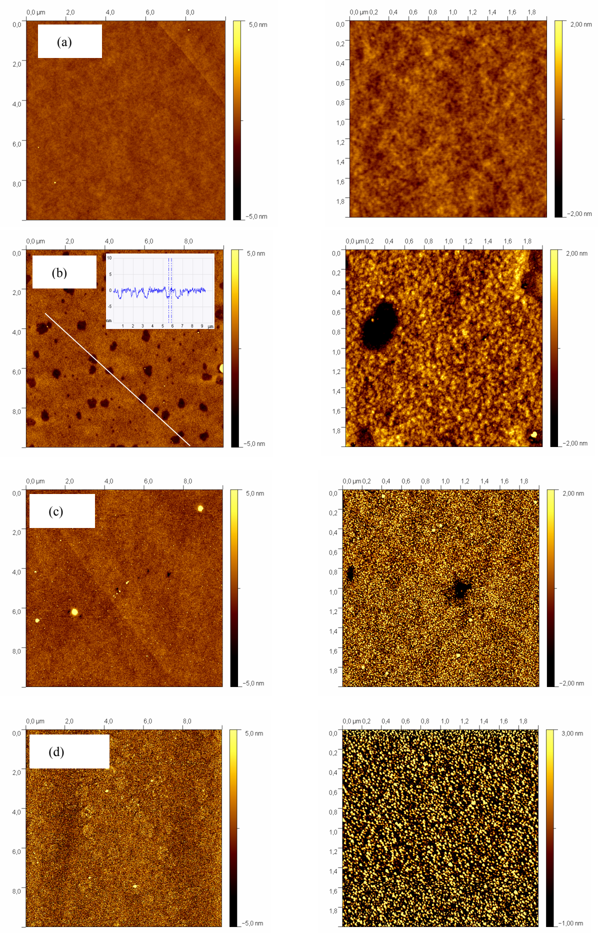

Fig. 7. 10 μm × 10 μm (left) and 2 μm × 2 μm (right) AFM images of Matrimid® 5218 surface: (a) untreated film, (b) CF_4 plasma treated film, (c) N_2 plasma treated film, (d) O_2 plasma treated film. Inset to Figure 6b: roughness profile of Matrimid® 5218 surface after the exposure to CF_4 plasma.

due to the introduction of polar groups onto the polyimide surface. So, XPS analysis was employed to identify those attached polar groups. After N_2 plasma treatment the C-C peak at 284.2 eV decreased, whereas peaks at 285.3 eV and 286.5 eV (attributed to C-N bond) increased significantly, most likely because of the incorporation of C-NH_x species (Fig. 6c). And really, the atomic concentration of nitrogen increased to 10 at.% and N/C ratio increased to 0.15 (0.05 for untreated membrane) (Table 2). As in the case of CF_4 plasma treatment, the disappearance of π-π* transition at 291.3 eV testifies to the attack of carbon-carbon double bonds of Matrimid® 5218 yielding to the nitrogen-containing functionalities. According to the literature, the formed nitrogen species may be attributed to C-N/C-CN_2 and C-N/N-CO groups.[38] At the same time, the initial oxygen content in the untreated Matrimid® 5218 membrane has increased from 12 at.% to 24 at.% (Table 2). This situation also indicates the functionalization with oxygen-containing species. The real oxidation level of the polyimide surface, expressed as O/C ratio, changes from 0.14 up to 0.36 (Table 2). As it was described previously, the exposure of the plasma treated surfaces to wet air enhances a post-plasma functionalization since many of the species generated during the plasma treatment are highly unstable and, as a consequence, have a great tendency to react.[28,36,38,39] Plasma treatment induces the formation of many free radicals which act as the basis for the interlocking of some particular functionality, i.e. oxygen-based groups.

O_2 plasma treatment causes variations in the XPS peak intensities and positions (Fig. 6d), which can be explained by the modification of the imide structure and the opening of benzene ring to form a linear carboxyl species.[19,33] It has been established that the atomic oxygen can react with the C-N bonds in polyimide, the weakest bond in this polymer, and form C-O-N bonds.[32] A significant increase of O/C ratio (up to 0.47, Table 2) confirms that important oxidation occurs in Matrimid® 5218 film during the plasma treatment. The C=O bond opens during the plasma treatment and generates the C-O and C-OH bonds.[19] It is known that C-OH bond is one of the important chemical bonds for the hydrophilicity improvement that agrees well with the results of the water contact angle measurements (Fig. 4 and Table 1).

AFM measurements. It is known that the hydrophilicity of the surface is improved not only by the chemical structure of the surface, but also by the effective surface area, i.e. by the surface roughness. To investigate this fact, the surface roughness of plasma treated films was studied by AFM measurements. Each AFM image was analysed in terms of arithmetic roughness (*Ra*) and characteristic grain size. Fig. 7 shows 10 µm × 10 µm (left) and 2 µm × 2 µm (right) AFM images of the surface of polyimide films after different plasma treatments.

The surface of untreated Matrimid® 5218 films is flat and homogeneous (Fig. 7a). Its roughness is equal to 0.2 nm and the average size of grains is around 5-15 nm (Table 3). As one can see from the results in Table 3, the roughness of the polyimide surface is increased by plasma surface treatment. In general, two competing processes occur during the plasma treatment. The first is the functionalization of the membrane surface by the creation of bonds (functions) characteristic of the gas used. This process is mainly quantified by measurements of the water contact angle and XPS analysis. The second process is the degradation (etching) of the film surface. These processes may occur either simultaneously or one process can dominate. In both cases they affect the morphology and the roughness of the film surface. This, in turn, can influence the wettability of the surface. In general, increasing roughness on a hydrophilic surface decreases the contact angle, whereas increasing roughness on a hydrophobic surface increases the contact angle.[22,32,33,40] As compared with the roughness of untreated Matrimid® 5218 film surface, there is a slight difference in roughness value for CF_4 plasma treated film (Table 3). However, CF_4 plasma treated surface shows a granular appearance with the average grain's size of 60 nm (Fig. 7b and Table 3). This result indicates that CF_4 plasma treatment can lead to the surface etching of polyimide films and form carbon-fluorine functional groups on the etched sites (Fig. 6b). The dark zones presented in the AFM image which may be attributed to the pinholes, are not the pinholes as, taking them into account, the value of arithmetical roughness *Ra* is not changing significantly, i.e. *Ra* equal to 0.48 nm is found for the total surface and *Ra* = 0.40 nm – without taking into account the dark zones (inset to Fig. 7b). Besides, the same topological changes of the polyimide surface, i.e. the presence of the grains with the average size of 60 nm, are found at the bottom of these zones and everywhere on the treated surface, whereas the untreated Matrimid® 5218 surface was flat and homogeneous with the average size of grains about 5-15 nm and the roughness equal to 0.2 nm. The surface morphology change of CF_4 plasma treated film should not be the main contributor to the significant increase of the water contact angle (Table 1). This observation leads to the idea that the change of surface chemistry on treated Matrimid® 5218 plays a predominant role in the increase of the water contact angle values.

Table 3. Roughness and average size of grains for plasma treated Matrimid® 5218 films.

	Untreated film	CF_4 plasma treated film	N_2 plasma treated film	O_2 plasma treated film
Ra (nm)	0.2	0.4	0.6	1.5
Average size of grains on surface (nm)	5-15	60	10-20	20-40

After N_2 and O_2 plasma treatments an increase of the surface roughness is observed, especially in the case of O_2 plasma modification (Table 3). The nitrogen plasma is not as aggressive as oxidizing plasmas, but the action of some species present in the plasma promotes chain scission as described above, and this can lead to etching, that is, changing in surface roughness (Fig. 7c and Table 3), which positively contributes to a wettability increase (Fig. 4 and Table 1). This indicates that sputtering effects are not homogeneous on the whole surface. However, since there is only a slight increase in the roughness of the plasma treated surface, the increase of wettability of Matrimid® 5218 film after the plasma exposure is attributed mainly to the effect of interaction plasma active species with the polyimide surface and to the formation of the polar groups. They are characterized by their high hydrophilic properties as it is seen from the XPS results (Fig. 6c).

On the other hand, there are significant changes in the morphology of the surface after O_2 plasma treatment, with the roughness value being the highest one (1.5 nm, Table 3). So, in this case the improvement in wettability of a surface may be attributed both to the increase of the surface roughness (Table 3) and to the formation of polar bonds in the surface region (Table 2). Surface roughening of polymer membrane can result from the difference in etching rates of different regions of the polymer during reactive ion etching.[23,31,34] The obtained results indicate that the large increase of arithmetic roughness *Ra* (Table 3) dramatically reduces the water contact angle values (Fig. 5). The complete water wetting is believed to be primarily caused by a large increase in surface roughness induced by the oxygen ion bombardment together with the formation of O_2 plasma generated functional groups. Really, O/C ratio was found to be the highest one in this case (0.47, Table 2). Surface micro-roughness produces a greater surface area that leads to increased total surface area and, as a result, to reduced contact angle values. However, is difficult to differentiate the effect of surface roughness and surface functional groups on the measured contact angle values.

Ageing effect. The ageing behaviour of the plasma treated Matrimid® 5218 films was studied using water contact angle

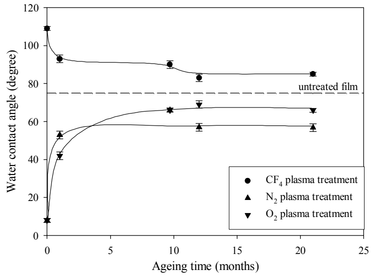

Fig. 7. Evolution of the water contact angle as a function of ageing time for plasma treated Matrimid® 5218 films.

measurements. After the plasma treatment, polyimide membranes were stored in the dessicator at room temperature (23 ± 2 °C). Fig. 8 shows the evolution of the contact angle of the plasma treated films as a function of storage time. As shown in Fig. 8, the ageing process is characterized by a change in the water contactangle values during first months of storage. The increase of the water contact angle is observed in the case of N_2 and O_2 plasma treatments and the water contact angle decrease – in the case of CF_4 plasma treatment. At a longer storage time, the contact angle changes more slowly and finally reaches the plateau value of 85 °, 57 ° and 66 ° for CF_4, N_2 and O_2 plasma treatment, respectively. It is suggested that the change in the contact angle can be explained by the phenomenon of orientation of mobile groups into the bulk of the material.[41,42] At the beginning, just after the plasma treatment, hydrophilic or hydrophobic groups are incorporated on the polymer surface and, as a result, the improvement of hydrophilic or hydrophobic properties is observed for freshly treated films. However, for the polymer films stored for some months, the functional groups starts getting reoriented toward each other and also toward the interior. It is because of this fact that the contact angle changes (Fig. 8). However, it should be highlighted that the contact angle value reached after the storage differs from the water contact angle value for untreated polyimide film (75 °), which means that the plasma surface modification is being kept even after 21 months of ageing.

Gas transport properties of plasma treated Matrimid® 5218 films

To evaluate a possible change of gas transport properties of plasma treated Matrimid® 5218 films, the values of permeability, diffusion and solubility coefficients towards N_2, O_2 and CO_2 through the polymer membrane were calculated according to Equation (1) – (3) (Fig. 9 and Table 4). The permeability values found for the untreated Matrimid® 5218 film (Table 4) are similar to those found in the literature.[43-45]

In general, the permeability coefficient of polyimide films for three studied gases (CO_2, N_2 and O_2) decreases in the following order [43,44] (Table 4):

$$P_{CO_2} \rangle P_{O_2} \rangle P_{N_2} . \tag{5}$$

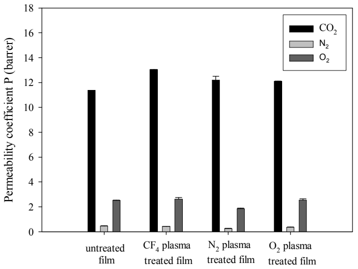

Fig. 9. Permeability coefficient of CO_2, O_2 and N_2 for plasma treated Matrimid® 5218 films.

Table 4. Gas transport properties of plasma treated Matrimid® 5218 films.

	Permeant	P (Barrer[a])	$D \cdot 10^8$ (cm^2/s)	$S \cdot 10^2$ cm^3 (STP)/cm^3/cmHg
Untreated film	N_2	0.46 ± 0.01	0.27 ± 0.02	1.73 ± 0.12
	O_2	2.50 ± 0.04	1.21 ± 0.01	2.08 ± 0.02
	CO_2	11.38 ± 0.01	0.70 ± 0.02	16.40 ± 0.60
CF_4 plasma treated film	N_2	0.42 ± 0.01	0.19 ± 0.01	2.20 ± 0.14
	O_2	2.61 ± 0.12	1.23 ± 0.14	2.15 ± 0.33
	CO_2	13.05 ± 0.01	0.66 ± 0.02	19.9 ± 0.5
N_2 plasma treated film	N_2	0.25 ± 0.01	0.17 ± 0.03	1.52 ± 0.24
	O_2	1.85 ± 0.03	0.87 ± 0.10	2.13 ± 0.21
	CO_2	12.21 ± 0.29	0.65 ± 0.02	19.00 ± 1.10
O_2 plasma treated film	N_2	0.36 ± 0.02	0.16 ± 0.01	2.28 ± 0.09
	O_2	2.54 ± 0.09	1.08 ± 0.02	2.34 ± 0.12
	CO_2	12.11 ± 0.01	0.60 ± 0.01	20.15 ± 0.64

[a] 1 Barrer = 10^{-10} cm^3 (STP) · cm/(cm^2 · s · cmHg)

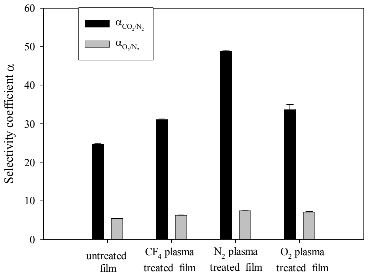

Fig. 10. Selectivity coefficients ($\alpha_{CO2/N2}$ and $\alpha_{O2/N2}$) of plasma treated Matrimid® 5218 films.

This order is also the order of increasing the kinetic molecular diameter of the penetrant gas (CO_2: 3.3 Å; O_2: 3.46 Å; N_2: 3.64 Å). As shown in Fig. 9, untreated and all treated Matrimide® 5218 films follow this succession. Besides, as one can see from Table 4 and Fig. 9; there are some slight changes of the permeability coefficient of the Matrimid® 5218 film after the plasma treatment, especially after N_2 plasma treatment. As the transport properties reflect the behaviour of the whole material and not only the surface characteristics, one may suppose that thebulk structure of the Matrimid® 5218 film was not affected by the surface plasma treatment, so that the gas permeation flow was not significantly modified. It is not surprising as it is known that the plasma treatment usually influences only the outermost layer of the polymer film.[8] Besides, it was found that the thermal and mechanical properties of the plasma treated membranes were the same as the properties for the untreated Matrimid® 5218 film.

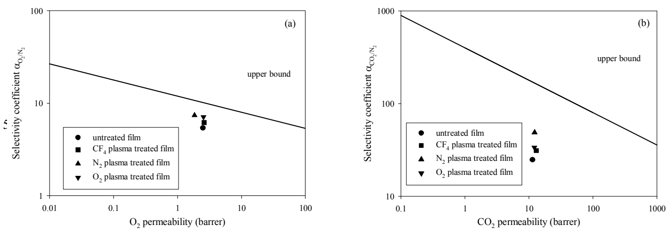

Fig. 11. Robeson plot of O_2/N_2 (a) and CO_2/N_2 (b) performance for plasma treated Matrimid® 5218 films.

In its turn, the selectivity coefficients of CO_2/N_2 and O_2/N_2 for untreated and plasma treated films are presented in Fig. 10. After the plasma treatment, the calculated selectivity coefficients are found to be higher (especially $\alpha_{CO2/N2}$) than those obtained for untreated Matrimid® 5218 film. This fact results from a selective permeability after plasma treatments (Table 4 and Fig. 9). Really, the decrease of the permeability coefficient towards N_2 and the slight increase of the permeability coefficient towards CO_2 after N_2 plasma treatment give rise to the increase of $\alpha_{CO2/N2}$ by more than 95 % compared to the untreated membrane (Fig. 10). On the contrary, the permeability coefficient towards O_2 after the plasma treatments stays practically invariable. Thus, one can observe that the outermost layer of a polymer membrane modified by a specific cold plasma treatment may cause a change in the gas permeability. This property can be used in the separation technology, when it is important not to change the bulk (i.e. mechanical) properties of the membrane.

To better understand the influence of the cold plasma treatment on the permeation properties of treated Matrimid® 5218 films, the diffusivity and solubility coefficients should be analyzed. Table 4 shows that diffusion coefficients for all plasma treated films are relatively close to those for the untreated membrane with a tendency of the diffusion coefficient decrease after the plasma treatments, especially after N_2 and O_2 plasma treatments. Besides, for all plasma treated films the solubility coefficients of all tested gases are slightly increased (Table 4).

With CF_4 plasma treatment the slight increase of the gas permeability can be attributed to the increase of solubility, especially for CO_2 permeant (Table 4), as the diffusivity is not really changed. As it was shown previously, during CF_4 plasma treatment the functionalization and degradation are the two competitive reactions. For the degradation process the atomic fluorine is responsible. Durrant et al. have shown that $[CF_x]/[F]$ ratio controls the balance between the functionalization and degradation processes.[46] The gas permeability behaviour of CF_4 plasma treated polyimide film depends not only on the degradation of the film surface (the presence of holes on the treated surface (Fig. 7b)), but also on the affinity of the fluorinated surface with the gas diffusing species, in particular with CO_2 permeant.[45]

In the case of N_2 and O_2 plasma treatments, the increase of the permeability coefficient for CO_2 can be explained by the presence of the functionalities, such as amine groups,[47] exhibiting high CO_2 affinities. That's why the significant rise of the selectivity coefficient of CO_2/N_2 is observed for these two plasma treatments, i.e. the increase by 36 % and 98 % for O_2 and N_2 plasma treated Matrimid® 5218 films, respectively. Moreover, Dmitriev et al. have shown that it is possible to increase the porous diameter of a membrane by power increasing during air plasma treatment.[48] So, the plasma treatment can be supposed to provoke the creation of the nanoporous structure that can be correlated with the increase of the surface roughness (Table 3). Indeed, in the case of O_2 plasma treatment the modified surface layer is not homogeneous, with the roughness value being the highest one (1.5 nm compared to 0.2 nm for the untreated membrane) (Table 3 and Fig. 7d). Besides, due to the action of oxidizing plasma the degradation effect is also present in this case. On the contrary, in the case of N_2 plasma treatment the homogenous dense layer is formed during the plasma treatment thus leading to the highest selectivity coefficient (Fig. 10). The difference between the structures of the plasma treated membranes is also seen from the ageing study (Fig. 8), i.e. N_2 plasma treated polyimide film preserves its hydrophilic properties longer in comparison with O_2 plasma treated film.

The trade-off between selectivity and permeability for gas separation is often represented on the Robeson plot.[49] So, the gas separation performance of the plasma treated membranes was plotted on the Robeson's upper bound plot in order to compare the results with the literature data (Fig. 11). As expected, all plasma treated membranes showed higher CO_2 permeability in comparison with untreated Matrimid® 5218 film. However, only N_2 plasma treated polyimide film revealed better permselectivity than untreated Matrimid® 5218 film.

Conclusion

The surface properties of Matrimid® 5218 film were modified by RF cold plasma treatment. Plasma parameters were optimized in order to obtain highly hydrophobic or hydrophilic surfaces. It was demonstrated that the water contact angle values depended strongly on the used plasma conditions. XPS and AFM measurements showed significant changes in chemical composition and topography of treated polyimide surfaces. XPS analysis confirmed the presence of the characteristic functional groups on the polymer surface. In the case of CF_4 plasma treatment these groups improve the hydrophobic character of the film surface, whereas in the case of N_2 and O_2 plasma treatments they give a pronounced hydrophilic character. The increase of the surface roughness of Matrimid® 5218 films after the plasma treatments was demonstrated by AFM measurements. The influence of the plasma treatment on the gas transport properties was evaluated. The increase of selectivity coefficients through Matrimid® 5218 film after the plasma treatments was found by the gas permeation measurements. It is supposed that the increase of gas flow is due to the affinity increase between the permeant and the treated polymer surface. In addition, solubility coefficient was found to be influenced by the plasma treatments. The obtained results allow this methodology to be used in many practical applications where highly hydrophobic/hydrophilic surface of polyimide is required.

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