

Atmospheric Pressure Plasma Jet Treatment of Polyethylene Surfaces for Adhesion Improvement

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Polyethylene (PE) samples were activated by an atmospheric pressure plasma jet. The improvement in adhesive bond strength is attributed to the incorporation of oxygen-containing functional groups into the PE surface. Optical emission spectroscopy in combination with XPS analysis shows differences in the surface reactions for a plasma jet operated with air or pure nitrogen. The results indicate that the surface modifications take place in two different environments with respect to location and time: (a) reactions while the substrate is hit by the plasma jet, and (b) reactions outside the plasma jet after the treatment.

Introduction

Many polymers, composite materials and metals need a pretreatment step before adhesive bonding or painting.^[1] The pretreatment modifies the surface properties of the substrate, thereby improving the adhesion strength and the durability of the adhesive joint. Low pressure and atmospheric pressure plasmas have found widespread use for the pretreatment in industrial applications.^[2] In particular, atmospheric pressure plasma jets (APPJ) gained large acceptance, because they are easy to integrate into existing production lines and they can treat specific parts of a substrate selectively.^[3,4] Also, in contrast to most corona treatments (and dielectric barrier discharges),^[5] APPJs are not limited to flat and thin substrates but can also be used for large three-dimensional structures.

For optimal performance, the process parameters of the treatment have to be determined for each application/material individually, since the plasma–surface interaction depends strongly on the substrate properties. Usually, the optimization process is a costly, time-consuming empirical approach. With the ultimate goal to improve the search for the optimal process parameters we studied the activation mechanism of polyethylene (PE) for a pretreatment with a commercial APPJ system used in many industrial applications. The substrate surface modifications are studied by surface analysis and adhesive bonding experiments. The plasma is characterized by optical emission spectroscopy. The use of this APPJ for the pretreatment of polymers and metals has been reported before by several authors.^[6–9]

Experimental Part

The polymer studied was a commodity ultrahigh-molecular-weight PE (PE-HMG 1000, Simona AG) obtained from Rocholl GmbH (Aglasterhausen, Germany). The samples size was 100 × 24.8 × 4 mm. The samples were cleaned by ultrasonic rinsing in iso-propanol for 30 s before use. A plasma jet system from Plasmatreat GmbH (Steinhagen, Germany) was used for the

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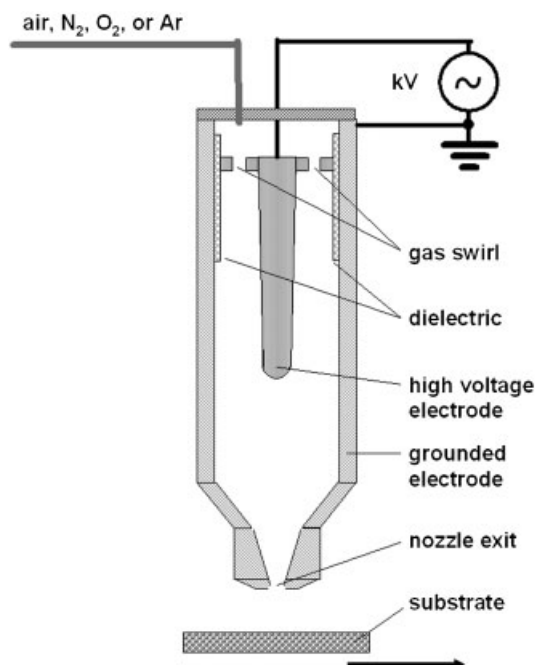


Figure 1. Schematic drawing of the plasma jet. The plasma was generated inside the nozzle and expelled through an orifice onto the substrate surface. The maximum possible treatment distance was 25 mm.

pretreatment (Figure 1).^[10] The jet was operated with either dry air or pure nitrogen (purity 99.999%, Linde AG) at an input pressure of 5.9 bar and a flow rate of $17 \text{ l} \cdot \text{min}^{-1}$. The excitation frequency for the plasma was between 17 and 22 kHz, with pulse peak heights of approximately 5 kV. The samples were moved on a translation stage through the plasma jet at a distance from the nozzle exit of 3 mm at a speed of $100 \text{ m} \cdot \text{min}^{-1}$ for a single treatment. This corresponds to an approximate treatment time of 5 ms.

Surface tension was determined from contact angle (CA) measurements (dynamic mode, advancing angle) with water, glycerol and diiodomethane as probe liquids using the approach of Owens–Wendt–Rabel and Kaelble.^[11,12] The AFM (Nanoscope III, Digital Instruments) was operated in the tapping mode with a resonance frequency of the sensor of around 250 kHz. XPS measurements were performed with a Kratos Ultra system with a

monochromatic Al K_{α} x-ray source and a pass energy of 20 eV for detailed spectra. The C1s peak was set to 285.0 eV. The surface analysis was carried out approximately 24 h after the plasma treatment.

For adhesive bonding, a two-component methacrylate adhesive (Araldite 2024) was used. This adhesive was chosen because it shows an adhesive failure mode in the non-treated state of the surface as well as after the pretreatment. Complications in the data evaluation due to cohesive failure modes are therefore minimized. The thickness of the adhesive layer was 0.1 mm with an overlap of 12.5 mm between the samples. The samples were allowed to cure for 2 d. Adhesive bond strength was measured by lap shear measurements according to DIN EN 1465.

The spectroscopic measurements were made with a miniature optic fibre spectrometer (USB2000, Ocean Optics Inc.) at a spectral resolution of 1.0 nm. The spectra are not corrected for detector sensitivity. The spectral line positions were assigned according to Pearse and Geydon,^[13] and the wavelength calibration of the spectrometer was performed with a mercury lamp.

Results and Discussion

The PE samples were pretreated by the APPJ with two different process gases (dry air and pure nitrogen). Table 1 presents the results of the contact angle (CA) measurements, adhesive bonding experiments, XPS and AFM measurements. The plasma treatment improves the adhesive bond strength of PE from 0.5 MPa to approximately 2 MPa. This improvement is interconnected with an increase in the surface tension and to the incorporation of functional groups containing oxygen and nitrogen into the PE surface. According to the AFM measurements, the plasma treatment does not alter the surface roughness significantly. Very similar effects of the plasma treatment with respect to surface roughness have also been observed for poly(vinylidene fluoride) and poly(ethylene terephthalate) in our group.^[8] This seems to indicate that the chemical composition of the surface is more important than surface roughness for adhesive bondability. This result corresponds to an adhesion mechanism according to

Table 1. Surface and adhesion properties of PE before and after APPJ treatment with air and nitrogen as process gas, respectively. Hydrogen atoms are neglected in the quantitative analysis of the XPS data. The RMS roughness from the AFM measurement was determined from a $2.5 \times 2.5 \mu\text{m}$ scanning area.

Treatment	CA water	Surface tension	Lap shear strength	AFM RMS roughness	XPS	
		$\text{mN} \cdot \text{m}^{-1}$	MPa	nm	O at.-%	N at.-%
Reference	93.3°	30.2	0.5	9.1	3.0	<0.1
Air plasma	21.6°	67.5	1.9	14.3	21.4	3.3
Nitrogen plasma	41.0°	55.3	2.1	11	16.9	5.4

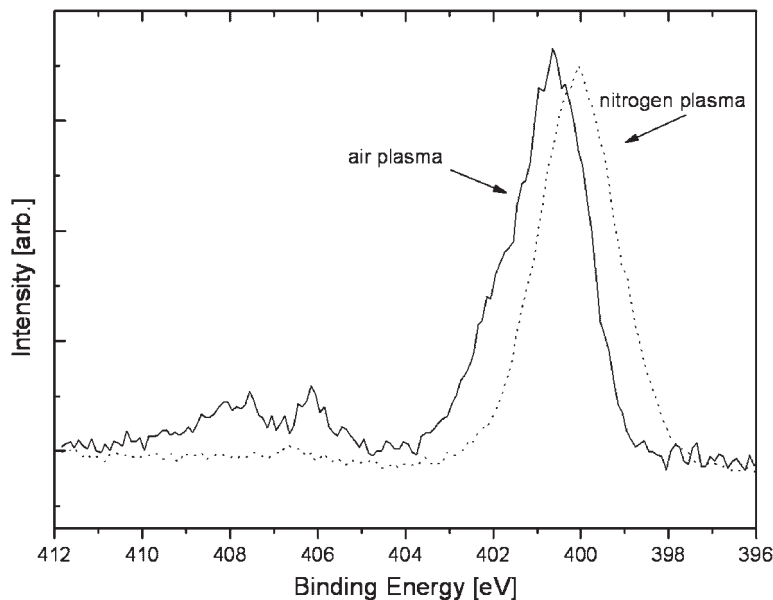


Figure 2. N1s XPS spectra of the PE surface after air (-) and after nitrogen (---) plasma treatment.

the chemical reaction theory, where dipole attraction and the formation of chemical bonds between the substrate and the adhesive is mainly responsible for the bond strength.^[14,15]

Using two different feed gases allows to obtain additional information on the activation mechanism. To study the conditions in industrial applications the experiments were carried out without a concealed environment around the sample and the plasma. Therefore, ambient air can interact with the sample and the plasma jet.

Comparison of the surface modifications after air plasma and nitrogen plasma treatment reveals several interesting aspects. Under otherwise identical process parameters the air plasma treatment leads to a higher surface tension than the nitrogen plasma. This seems to be caused by the higher total concentration of heteroatoms, especially oxygen, incorporated into the substrate surface of the air plasma treated sample. In spite of the lower surface energy, the nitrogen plasma sample yields a better bond strength however. This effect is well known and confirms the absence of a direct correlation between surface tension and bond strength.^[1,15]

As discussed, the total number of incorporated heteroatoms (O, N) is slightly higher for the air plasma treatment than for the nitrogen plasma treatment (21.7 and 19.3 at.-%, respectively).^a As one would expect, the surface concentration of nitrogen is higher after the nitrogen

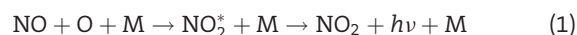
^a The initial amount of 3 at.-% oxygen, possibly due to additives and contaminants, has been subtracted.

plasma treatment. However, noteworthy is the large amount of oxygen that is found in the nitrogen plasma treated sample. There are three major possibilities for the origin of the oxygen content: (i) diffusion of oxygen or water vapour into the nitrogen plasma jet and subsequent incorporation into the substrate surface while the sample is hit by the plasma; (ii) reactions of the substrate surface with the ambient atmosphere after the plasma treatment; (iii) a combination of both effects.

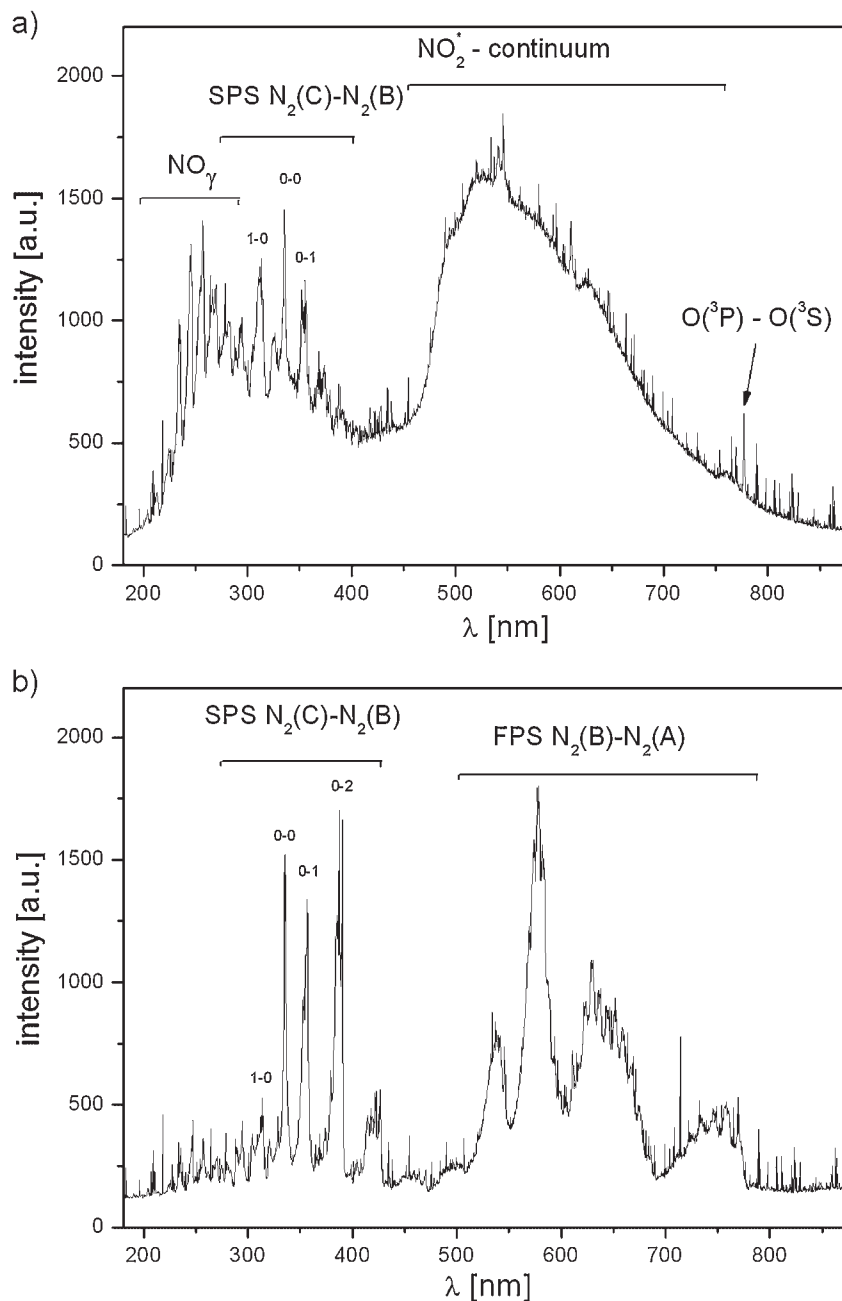
XPS spectra of the N1s region reveal further differences between the air plasma and the nitrogen plasma treatments (Figure 2). For the following analysis, we use the peak assignment employed by Lynch et al.^[16] The nitrogen plasma leads predominantly to the formation of reduced nitrogen species (NH₂, and nitrile around 400.0 eV) in the PE surface. This is surprising since also large quantities of oxygen are found in the substrate surface. In contrast, the N1s XPS spectrum after air plasma

treatment shows the formation of oxidized nitrogen species (features around 406.2 and 408.0 eV attributed to NO₂ and NO₃ functional groups) and a shift of the N1s line maximum to 400.7 eV (oxim, imine and amide species). The formation of those functional groups can be readily explained by the simultaneous existence of reactive oxygen and nitrogen species in the air plasma. These differences in the N1s XPS spectra indicate that different plasma–surface reactions take place for an air and a nitrogen plasma jet treatment.

To further study the origin of the oxygen uptake for the nitrogen plasma treated sample, OES has been used to characterize the APPJ. The emission was collected from the region of the relaxing plasma jet that is traversed by the substrate for the treatment (i.e., in a distance of about 3–4 mm from the nozzle outlet). Figure 3 presents the emission spectra of the air and the nitrogen plasma. The spectrum of the air plasma is dominated by bands of NO (NO_γ – system, λ = 200–290 nm), N₂ molecules (second positive system SPS, λ = 290–410 nm), excited O atoms (at λ = 777.4 nm), and the yellow continuum emission of excited NO₂ molecules (λ = 450–800 nm). This characteristic emission of NO₂ is generated by the chemiluminescence reaction^[17,18]



where M is any third partner (N₂, O₂, ...). In contrast, the nitrogen plasma radiation does not contain any emission from oxygen species. Only emission of N₂ arising from the SPS [N₂(C) → N₂(B)] and of the first positive system FPS [N₂(B) → N₂(A) at λ = 600–700 nm] is observed. However,



■ Figure 3. OES spectra of the relaxing plasma of the APPJ with different process gases: (a) dry air and (b) nitrogen.

since OES detects only emitting species, the existence of oxygen species in the nitrogen plasma cannot be ruled out completely. A more detailed analysis of the emission spectra and an estimation of the amount of oxygen atoms in the remote plasma on the basis of a kinetic model has been given by Wagner et al.^[19]

From the combination of the spectroscopic results and the surface analysis data, the following rough picture of the activation mechanism emerges: the air plasma treatment causes modifications to the PE surface by

plasma–surface reactions arising from plasma species like electronically excited NO₂, NO, O and N₂. This explains the features for the oxidized nitrogen species in the N1s XPS spectrum and accounts for the overall amount of oxygen and nitrogen in the substrate surface. The absence of optical spectral features from oxygen species in the nitrogen plasma jet indicates that no or only a small amount of oxygen species diffuse into the plasma jet or become electronically excited. This explains the absence of NO_{x=2,3} features in the XPS spectrum and the absence

of $\text{NO}_{y=1,2}$ features in the optical emission spectrum. However, to explain the large oxygen concentration of approximately 17 at.% in the PE surface it seems very likely that post-plasma reactions take place, where ambient oxygen species react with the surface. In addition, oxygen species that are not visible in the OES, can react with the PE surface while the substrate is in the plasma. The post-plasma reactions are very likely caused by stable radical sites formed by UV radiation from the plasma or excited nitrogen molecules. Such post-plasma reactions have been observed in many low-pressure plasma treatments and are usually attributed to the existence of long-lived radical sites in the substrate surface.^[14,20] In addition, a replacement of imine groups by oxygen via hydrolysis by atmospheric water could contribute to the oxygen uptake, as suggested by Foerch et al.^[21] and by Gerenser.^[22] To quantify the extent of such plasma reactions for this APPJ treatment, additional experiments with a controlled gas atmosphere are underway.

Conclusion

APPJ treatment with air and nitrogen improves the adhesive bond strength of PE by chemical modifications of the surface. OES shows the formation of NO_x species and excited N_2 molecules in the relaxing air and nitrogen plasma, respectively. Those differences lead to different surface modifications with respect to nitrogen functionalities for both types of plasma jet treatment. The results indicate that for a detailed understanding of the activation mechanism for this APPJ system not only the plasma-surface reactions need to be taken into account but also post-plasma processes with the ambient gas atmosphere. Theoretical predictions of the optimal process parameters by plasma chemistry modelling thus become more difficult because additional reactions which are not directly related to the plasma treatment need to be considered.

Acknowledgements: The authors gratefully acknowledge *Michael Noeske* and *Christian Tornow* for their AFM and XPS measurements.

Received: September 8, 2006; Revised: November 29, 2006;
Accepted: December 5, 2006; DOI: 10.1002/ppap.200732402

Keywords: adhesion; modification; optical emission spectroscopy (OES); plasma jet; polymer treatments; surface modification

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